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Department of Chemical Sciences



Ph.D. in Chemical Sciences

Design and development of solid-state

functional materials for Na-ion batteries



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Abstract

This Thesis addresses new functional materials for Na-ion battery (NIB) applications. Since the breakthrough of Li-ion battery (LIB), extensive research has been focusing on alternatives to Lithium, based on cheaper and widespread elements for sustainable energy storage solutions. In this context, the effective large-scale deployment of NIB requires great efforts in the development of good Na⁺ host anodes, high-energy cathodes and safe electrolytes. New components must ensure enhanced efficiency in the NIB operating processes (*i.e.*, Na^+ insertion/extraction at the electrode/electrolyte interface and Na⁺ transport through the electrolyte) for empowering high energy density and long-term cycle stability. Here, we present NIB materials optimization through an innovative approach, based on computational methods that are directly related to experiments. Our aim is to unveil the most important features that can affect the material capabilities towards Na⁺ uptake, transport and storage. During the research activity at Università di Napoli Federico II, state-of-the-art DFT methods have been employed to investigate the structure-property relationship of solid-state nanoelectrodes. Our studies on ${\rm TiO}_2$ anatase and MoS_2 /graphene 2D-heterostructure reveals that sodiation mechanisms are driven by intrinsic structural features. Migration barriers are directly correlated to structure-dependent descriptors, such as the accessible area for the intercalating $\mathrm{Na^{+}}$ at TiO_{2} surfaces, and the S coordination around the migrating Na^+ within MoS_2 /graphene interface. From these outcomes, we provide new design strategies to improve the electrode efficiency upon so diation, for example suggesting the preferential growth of ${\rm TiO}_2$ along the (001) direction or the introduction of S vacancies in MoS₂ monolayers. On the cathode side, we unveil the charge compensation mechanism occurring in $Na_x Ni_{0.25} Mn_{0.68} O_2$ upon desodiation, with a major focus on the O-redox chemistry at very low Na loads. Molecular O_2 is predicted to be released from Mn-deficient sites in the bulk cathode via formation of superoxo-species and preferential breaking of labile Ni-O bonds. We prove that increasing M-O covalency via suitable doping would prevent O_2 loss and allows to fully recover a reversible process. Research stages at ENS de Lyon and the R&D laboratory of Lithops s.r.l. have been dedicated to the optimization of electrolyte materials. By development and application of polarizable force fields in molecular dynamics simulations, we report reliable predictions of Na⁺ diffusion and solvation properties into the PyrFSI room-temperature ionic liquid (RT-IL). We combine RT-ILs with crosslinked PEO matrix to obtain highly conductive polymeric membranes. Galvanostatic cycling of Na metal based cells containing these innovative polymer electrolytes and state-of-the-art electrodes shows promising performances and paves the route to further assessment of efficient cells. The foreseen integration of these studies will provide new understanding on the complex charge transfer processes occurring at the electrode/electrolyte interface during battery functioning. The new knowledge on electrochemical behavior of advanced materials will be key for boosting the NIB technology in the near future.

Abbreviations

ASW	Anodic Stability Window		
BBPLED	Bipolar Pulse Longitudinal Eddy current Delay		
BJ	Becke Johnson		
BZ	Brillouin Zone		
CB	Carbon Black		
CBM	Conduction Band Minimum		
CC-Al	Carbon Coated Aluminum		
CD	Charge-density Difference		
CI-NEB	Climbing-Image Nudged Elastic Band		
CL&P	Canongia-Lopes & Pádua		
\mathbf{CN}	Coordination Number		
CNC	Cellulose Nano Crystal		
CSW	Cathodic Stability Window		
\mathbf{CV}	Cyclic Voltammetry		
DC	Drude Core		
DFT	Density Functional Theory		

DOSY	Diffusion Ordered Spectroscopy
DP	Drude Particle
EELS	Electron Energy Loss Spectroscopy
EES	Electrical Energy Storage
EIS	Electrochemical Impedance Spectroscopy
Emi	1-Ethyl 3-Methyl Imidazolium
EO	Ethylene Oxide
ESW	Electrochemical Stability Window
FSI	bis (Fluoro Sulfonyl) Imide
\mathbf{GC}	Galvanostatic Cycling
GGA	Generalized Gradient Approximation
GIC	Graphite Intercalation Compounds
GTO	Gaussian Type Orbital
HC	Hard Carbon
HER	Hydrogen Evolution Reaction
HF	Hartree Fock
HSE	Heyd Scuseria Ernzerhof
KS	Kohn Sham
LAMMPS	Large-scale Atomic Molecular Massively Parallel Simulator
LDA	Local Density Approximation
LIB	Li Ion Battery
MC	Monte Carlo
MD	Molecular Dynamics
MEP	Minimum Energy Path

\mathbf{ML}	Monolayer
MM	Molecular Mechanics
MO	Molecular Orbital
MSD	Mean Square Displacement
NIB	Na Ion Battery
NMR	Nuclear Magnetic Resonance
NNMO	$\mathrm{Na}_{x}\mathrm{Mn}_{0.68}\mathrm{Ni}_{0.25}\mathrm{O}_{2}$
NP	Nanoparticle
NVPF	$Na_3V_2(PO_4)_2F_3$
PAW	Projector Augmented Wave
PBC	Periodic Boundary Conditions
PBE	Perdew Burke Ernzerhof
PC	Propylene Carbonate
PDF	Pair Distribution Function
PDOS	Projected Density of States
PES	Potential Energy Surface
PEO	Poly (Ethylene Oxide)
PET	Poly (Ethylene Terephthalate)
PFGSE	Pulsed Field Gradient Spin Echo
PP	Poly (Propylene)
PVdF	Poly (Vinylidene Fluoride)
$Pyr_{13/14}$	N,N-methyl propyl/buthyl Pyrrolidinium
\mathbf{PW}	Plane Waves
RDF	Radial Distribution Function

RT-IL	Room Temperature-Ionic Liquid		
SAPT	Symmetry Adapted Perturbation Theory		
SCF	Self Consistent Field		
SDF	Spatial Distribution Function		
SEI	Solid Electrolyte Interphase		
SIE	Self Interaction Error		
\mathbf{SS}	Stainless Steel		
\mathbf{SQS}	Special Quasi-random Structure		
\mathbf{sXAS}	Soft X-ray Absorption Spectroscopy		
TFSI	bis (Tri Fluoromethane) Sulfon Imide		
\mathbf{TM}	Transition Metal		
TMDC	Transition Metal Dichalcogenide		
VASP	Vienna Ab-initio Simulation Package		
$\mathbf{v}\mathbf{d}\mathbf{W}$	Van der Waals		
VFTH	Vogel Fulcher Tammann Hesse		

1 Introduction

Sustainability, biocompatibility and decarbonization are some of the most relevant keywords of modern society. The awareness of energy problem is rising transversally in the industrialized world, involving both people daily life and political decisions. Recycling, low-energy consumption and limitation to plastic waste are essential bottom-up actions, as well as proper environmental policies are required to drive the economy and fund the research toward the transition to a sustainable society. It has been estimated that the current rate of energy production should be doubled by 2050 in order to face the energy demands of the ever-growing global population, achieving $130\,000\,\mathrm{TW}\,\mathrm{h}$ or the equivalent of 10^{10} tons of oil yearly [1–3]. This dramatic forecast demands the pursuit of renewable energy resources and sustainable storage technologies. The zero CO_2 emissions scenario must therefore become an imperative. Scientific community plays an active role in this process and researchers from several fields can contribute to assess advanced technologies able to store and convert clean energy. Chemistry and material science can support the worldwide efforts in this perspective, enabling the understanding of working principles and the design of efficient components. The activity carried out during the Ph.D. project and reported in this Thesis deals with this context, aiming to provide new chemical insights on how the structural features of case-study materials determine the physico-chemical properties of interest for energy applications. Electrochemical devices at the forefront in this research field are briefly presented in Section 1.1, while more detailed description is dedicated to Sodium-ion batteries in Section 1.2, with special focus on the key issues concerning materials development.

1.1 Electrical energy storage systems

The chance to enable the reversible electrical-to-chemical energy conversion has been powering the technological progress of modern society in a multitude of applications. Among electrical energy storage (EES) systems, rechargeable batteries cover a widespread portion of the market. The lead acid battery technology is more than 150 years old, cost-effective, and largely used in automotive applications and for auxiliary power supply, but its energy density is limited to \sim 30-40 W h kg⁻¹ and the energy efficiency is normally low. Ni-based chemistries have also been successful in different devices, such as the Ni-Fe, Ni-Zn and Ni-Cd batteries, where the NiOOH/Ni(OH)₂ cathode system is combined to Fe, Zn and Cd metal anodes, or the Ni-H₂ and NiMH batteries, employing hydrogen and metal hydrides as negative electrodes and showing practical energy densities of

 $\sim 100 \,\mathrm{Wh\,kg^{-1}}$. More recently, the development of Lithium-ion batteries (LIBs) have had a huge technological and social impact, as recognized by the 2019 Nobel Prize in Chemistry [4, 5]. Thanks to their high energy density, LIBs have quickly started to dominate the market and made the portable consumer electronics the main driver of their development. Since their commercialization, the energy density has continuously increased $(\sim 7-8 \text{ W} \text{h} \text{kg}^{-1} \text{ per year, reaching about } 250 \text{ W} \text{h} \text{kg}^{-1} \text{ today and being}$ almost close to its intrinsic limit, *i.e.*, 300 kW h [6]), and cell costs decreased much faster than expected (from $\sim 1000 \in /kWh$ in 1990s to ~ 200 \in /kW h today [7]). Lately, the urgent need for green economy is pushing the production of sustainable EES systems on a very large scale and other applications have put battery research in the spotlight, such as eco-friendly electric vehicles (EVs) and stationary electrical grids. The latter represent the key enabler for an effective use of renewable sources with intermittent nature, allowing to store and deliver excess energy supplied by wind and solar power on demand [3, 8]. Critical resource issues related to the scarce availability and the restricted geographical distribution of Lithium and some other components of LIB, especially Cobalt, are expected to hinder the integration of LIB in large-scale applications like EVs or smart grids. Creating new options for future energy storage is therefore of strategic relevance [9] and different battery chemistries are currently studied, joining the general aim to increase energy density $(Wh kg^{-1})$ or decrease costs (EUR/kWh) compared to state-of-the art LIB technology. Other relevant

parameters should be taken into account, such as safety, cycle and calendar life, operating temperature window [10]. In the following section, Sodium-ion batteries are presented as valid alternative in this context and the basic ideas behind the Lithium-to-Sodium transition are illustrated.

1.2 Na-ion batteries: challenges and perspectives

Since the breakthrough of Li-ion battery (LIB) technology, extensive research in both academia and industry has been focusing on alternative chemistries [11, 12]. The objective is replacing most dominating Li-ion based technologies with cheaper and widespread resources (e.q., Sodiumor Magnesium-based batteries) [13-17] that can boost the deployment of EES systems in large-scale applications [18-20]. Thanks to easily available sodium raw materials, Na-ion battery (NIB) devices are foreseen to be a key enabler for the transition to a more sustainable society: from large grid facilities, in combination with renewable energy conversion plants, to even futuristic electric transportation [3]. When fabricated in all-solid-state configuration, NIB devices would also meet the cost and safety requirements that are essential for their deployment in the market [21, 22]. Great advances in NIB research have been achieved owing to the neat similarities with state-of-the-art Lithium cells. As for LIBs, the cell chemistry is based on the insertion/extraction of sodium ions (*i.e.*, sodiation/desodiation) occurring at the interface of anode/cathode with the electrolyte upon charge/discharge. The electrode materials act therefore as host structures

in the reversible Na⁺ uptake and storage, while the electrolyte ensures the efficient ionic diffusion between them. Figure 1.1 shows a pictorial representation of these microscopic processes. Inspired by working principles similar to LIBs, significant efforts have been devoted to the design of efficient NIB component materials starting from electrodes and electrolytes of Li-based cells [23]. However, the differences between Li⁺ and Na⁺ ions (e.q., electrochemical potential, ionic radius) have revealed that, in most cases, sodium-analogues of state-of-the-art LIB materials do not represent a satisfactory solution [24, 25]. While the large Na⁺ radius helps in the diffusion through liquid electrolytes, it hampers a convenient Na⁺ reversible storage into the structure of the electrodes [26]. The consolidation of NIB technology strictly relies on enhanced energy density and stability to be achieved via high-performing Na⁺ host materials and safe Na⁺ conductors [25–28]. As shown in Figure 1.1, a conventional configuration in a LIB device features a graphite negative electrode and a layered ${\rm LiCoO}_2$ cathode material. The electrode reactions occurring in the cell are:

- negative electrode:

 ${\rm LiC_6} \longrightarrow {\rm Li}^+ + 6 \, {\rm C} + {\rm e}^-$

- positive electrode:

 $2\,\mathrm{Li}_{0.5}\mathrm{CoO}_2 + \mathrm{Li}^+ + \mathrm{e}^- \longrightarrow 2\,\mathrm{Li}\mathrm{CoO}_2$

- overall reaction:

 $LiC_6 + 2Li_{0.5}CoO_2 \longrightarrow 6C + 2LiCoO_2$



Figure 1.1: Scheme of the working principle of a Lithium-ion battery with Lithium ions intercalating into two host structures, here graphite and $LiCoO_2$ as example. A Sodium-ion battery can work the same way but the increase in ion size leads to significant changes in the cell behavior. Adapted from Ref. [29] with permission of John Wiley & Sons, Inc.

What is relevant for obtaining a high cell voltage is to combine two suitable intercalation compounds: one anode material for which the reaction with Lithium metal only releases little energy (redox potential close to Li/Li⁺ = 0 V, for example the intercalation of Li⁺ into graphite at below 0.25 V vs. Li/Li⁺), and another one serving as cathode, for which the reaction with Lithium metal releases a large amount of energy (redox potential much more positive than Li/Li⁺ = 0 V, such as the intercalation of Li⁺ into layered Li_{0.5}CoO₂ close to 4 V vs. Li/Li⁺). The same arguments hold for Sodium and any other intercalation system. The cell voltage, E, is determined by the Gibbs energy change of the cell reaction, ΔG , according to the well-known equation:

$$E = -\frac{\Delta G}{zF} \tag{1.1}$$

with z being the number of transferred electrons and F the Faraday constant. The intercalation potentials are highly structure-dependent and generally lower for Na⁺ than for Li⁺. This is observed for both positive and negative electrodes, so whether the cell voltage of a NIB is higher or lower compared to a LIB analogue depends on the intercalation/deintercalation efficiency at both electrodes.

For what concerns anode materials, early research efforts have started from the need to replace graphitic materials, since the structure is not suitable to reversibly accommodate Na⁺ cations [26, 30]. The performance of graphite in LIB is quite outstanding and it can be considered the almost exclusive anode material in commercialized LIBs. With Lithium, graphite forms a series of intercalation compounds (GICs) at potentials below 0.25 V vs. Li/Li⁺, leading to the final composition LiC₆ (372 mA h g⁻¹) [31]. Sodium does not form any Na-rich GICs, which is puzzling because GICs for the even larger Potassium and Rubidium alkali metals are well-known [32–34]. The underlying reason is still unclear. Disordered carbons, such as hard carbons (HC), have shown good sodiation activity, with reversible capacities of around 300 mA h g⁻¹ [35–38]. The microstructure and composition depend on the synthetic pathways, thus leading to different shapes in the voltage profiles. The overall storage behavior of Li and Na in HC

is similar, with one sloping region related to ion insertion between the disordered graphene layers, and one plateau region ascribed to ion storage by adsorption in micropores [39]. Another promising route for storing Lithium and Sodium is alloy formation with metals of the Groups 13, 14, and 15. Full lithiation of Silicon $(Li_{15}Si_4)$ or Tin $(Li_{15}Sn_4)$ corresponds to capacities of $3578 \,\mathrm{mA}\,\mathrm{h\,g^{-1}}$ and $847 \,\mathrm{mA}\,\mathrm{h\,g^{-1}}$, which is significantly higher than conventionally used electrode materials [40]. Formation of Li-based alloys takes place at potentials below 1 V vs. Li/Li⁺, while the average sodiation potentials are $0.15 \,\mathrm{V}$ lower [41]. In case of Silicon, this means that the sodiation potential for the formation of the NaSi inter-metallic phase $(954 \,\mathrm{mA}\,\mathrm{h\,g}^{-1})$ is very close to the metal plating potential. Large volume expansion, insufficient SEI formation and large initial irreversible capacity are the main drawbacks observed in alloy-based cells. Titanium oxides are capable of reversibly intercalating Li and Na at low redox potentials without undergoing conversion reactions. After Iron, Titanium is the second most abundant transition-metal and thus a very interesting element in view of resources. The redox potential for Sodium insertion into Na₂Ti₃O₇ is more than one volt lower than compared to Lithium insertion into Li₂Ti₃O₇ (0.3 V vs. Na/Na⁺ and 1.6 V vs. Li/Li⁺, respectively), meaning that the driving force for ion intercalation is much smaller in case of Na [42]. In situ studies during sodiation of $Na_2Ti_3O_7$ have confirmed that $Ti^{3+/4+}$ is the active redox couple [43]. The compound is able to store two Na⁺ to form Na₄Ti₃O₇ during discharge, corresponding to a theoretical capacity of $178 \,\mathrm{mA}\,\mathrm{h\,g}^{-1}$. Also protonated titanates and TiO₂ have shown promising results toward Na storage [44–46]. In all these families of materials, nanosizing has become a popular approach to improve the charge transfer kinetics. The thorough design of anode materials in the form of nanostructures would endow the electrodes with high reversible capacity, enhanced rate capability, and prolonged durability [47]. Herein, rational design strategies for the development of nanostructured anodes have been addressed through the investigation of Na⁺ intercalation and migration processes at the atomistic level. Chapter 2 is meant to show the main outcomes from our studies on two promising negative electrodes for NIBs, *i.e.*, TiO₂ anatase and 2D-MoS₂/Graphene heterostructure. Key issues in the search for positive electrodes involve enhanced energy

Rey issues in the search for positive electrodes involve enhanced energy density, structural stability at high operating voltage and cheap raw materials as cathode materials usually determine the manufacturing costs of the device. There are mainly two families of high-energy cathodic materials: layered transition-metal oxides and polyanionic compounds. The simple replacement of state-of-the-art LiCoO₂ with NaCoO₂ has led to impractical outcomes due to complex electrochemical behavior and critical phase transformation occurring upon desodiation [48]. However, the properties of NaTMO₂ oxides can be easily tuned via TM doping. In view of element abundance, Fe- and Mn-rich compounds are the preferred choice for NIBs [49, 50]. Polyanionic compounds with olivine-type structures usually show good phase stability during cycling at high operating voltages. The outstanding performances reported for LiFePO₄ have spurred the investigation of NaFePO₄ counterpart, but smart synthetic strategies are required to avoid the formation of the electrochemically inactive maricite phase [51]. In Chapter 3, we describe and discuss our atomistic investigation on a promising high-energy cathode for NIBs, *i.e.*, $Na_xNi_{0.25}Mn_{0.68}O_2$, and the design strategies that have been outlined in order to enhance the reversible capacity at high voltage.

The need to replace conventional organic electrolytes arises from early attempts to produce safe Li metal batteries with high energy and power densities that can be suitable for electric transportation. The high reactivity of volatile and flammable organic solvents with metallic Lithium leads to poor performance and uneven dendritic anode deposition, which could easily cause fire or explosion of the battery upon short-circuit. Similar safety hazards have also been reported in LIB prototypes employed in laptop PC and cell phones, even in the absence of the Li metal anode [52]. Great efforts have been dedicated to the development of alternative electrolyte materials, aiming to assure safety and durability that should be addressed in NIB research as well. Single-ion conductors [53], solid solutions [54], composites [55], and polymer or gel-polymer electrolytes [56-58] have been proposed as suited options to this purpose. A crucial aspect is represented by the extremely low stability of most electrolytes at low potentials, leading to chemical decomposition and formation of surface films. This interface must be electronically insulating but permeable for the cations in order to passivate the electrodes and stop the electrolyte decomposition. The film should be also sufficiently thin and flexible to survive the volume changes of the electrode during cycling. Achieving such a stable solid electrolyte

interphase (SEI) is therefore crucial for obtaining a reversible electrode reaction. The mechanisms of SEI formation are very complex and they can vary when moving from Lithium to Sodium. The SEI composition strongly depends on the electrolyte formulation (solvents, conductive salt, additives), which can be very different between LIB and NIB. Overall, the knowledge on the SEI in NIBs is still comparably small and further studies are needed to identify the relevant factors for obtaining an optimized SEI that is stable for a long time and over many cycles. All-in-all, the research for novel electrolytes is mainly driven by safety, reliability and recyclability concerns that set foundation for the large-scale deployment and industrialization of Na-ion batteries. In this Thesis, we have focused on innovative electrolytes based on room-temperature ionic liquids (RT-IL) and polymeric membranes that meet these requirements, as discussed in Chapter 4. On one hand, the understanding of ionic transport in complex RT-IL matrix has been addressed from both theoretical and experimental point of views. Molecular dynamics simulations and physico-chemical characterizations have been set up to describe diffusion and solvation properties of the Na^+ into RT-ILs medium. On the other hand, advanced preparation techniques of stable and conductive polymer electrolytes and corresponding electrochemical testing in lab-scale NIB prototypes has been performed to assess the electrochemical behavior of these promising materials.

Research on Sodium-ion batteries has become very dynamic, and fast progress in materials development and performance has been achieved. To commercialize NIBs, specific advantages over LIBs or other established

types of batteries are required. Cost-efficient batteries based on abundant elements might become relevant in the near future in order to face the great challenge of resource and chains supply for LIBs. From the scientific and chemical point of view, main contributions should be provided by investigating the efficiency of host electrode materials toward Na uptake and storage and the electrochemical stability of Na conductive electrolyte systems. We have briefly discussed the key issues for the Lithium-to-Sodium transition. In many positive electrode materials, replacement of Li by Na leads to a more complex behavior as additional intermediate phases form during cell cycling. For the negative electrode, the choice so far is limited, as graphite only stores Sodium under special circumstances and Silicon seems to be largely inactive. Other alloys, Titanium oxides and a variety of carbon materials are therefore intensively studied, though a much better understanding of the SEI formation is required. Overall, numerous and unexpected surprises have been found and much remains to be discovered. This also includes the use of Sodium in solid-state, metal/air- and metal/sulphur batteries. The race is on to enlighten fundamental understanding and identify novel materials with improved properties, thereby creating new options for future energy storage devices.

2 Ion intercalation and migration in nanostructured anodes

In the development of negative electrodes for Na-ion batteries, the most important requirement is certainly represented by the material structure and its mechanical response to a significant stress, *i.e.*, the Na⁺ intercalation. On one hand, the anode structure should feature suitable intercalation sites for the large Na⁺. Easily tunable materials have therefore attracted great interest, such as carbon matrix or 2D heterostructures. On the other hand, the crystalline network must be robust in order to retain its shape upon subsequent sodiation/desodiation. Advanced nanoengineering techniques have started to dominate this field and all the materials that can be easily produced and tuned at the nanoscale offer the chance to prevent huge volume variation upon cycling. Moreover, the high surface/volume ratio in nanomaterials greatly enhances the kinetics of ion diffusion and charge transfer processes at the electrode/electrolyte interface. The computational approach can be extremely beneficial in this context. State-ofthe-art quantum mechanics methods allow the material modeling at the nanoscale and the investigation of structure-property relationships that are relevant to improve the performances. Electronic structure analysis and atomistic details on the intercalation process are shown to be essential to outline rational design strategies for functional materials that can be used as highly performing anodes in NIBs.

2.1 A model for TiO_2 anatase nanoelectrodes

Titanium dioxide (TiO₂) is a versatile functional material with several applications, ranging from solar cells to photocatalysis and batteries [59, 60]. In the form of anatase, TiO₂ shows comparable performances to graphitic materials in LIBs, such as high reversible theoretical capacity (335 mA h g⁻¹), low volume variation upon cycling (less than 4%) and improved safety thanks to the structural robustness and high working potential. However, it still suffers from poor electrical conductivity ($\sim 1.9 \times 10^{-12}$ S m⁻¹) and slow ion diffusion [61]. Combining TiO₂ with conductive materials (*e.g.*, Graphene, mesoporous carbon, carbon nanotubes, other metal oxides) is effective for enhancing electronic conductivity [62, 63], while nanoengineering is important to favor diffusion kinetics thanks to short ion

diffusion pathways and large electrode/electrolyte contact area [64]. Recent efforts have been devoted to the development and scale-up of nanostructured TiO₂-based materials to be applied as negative electrodes in lab-scale NIBs [65–70]. Innovative synthetic strategies have been developed aiming to the advanced functionalization of TiO₂ nanoparticles (NPs) with carbon coating, thus enhancing the overall performance. Even if present in mixed formulation, TiO_2 still represents the active material, with other components being added in very small amounts [71]. So far, this material represents a highly promising choice for the overall balance of efficiency, stability and costs. Still, structural features, both in terms of crystallinity and morphology, seem to be crucial in determining the activity of TiO_2 NPs. For example, the work by Longoni *et al.* [69] proves that the performances of anatase NPs as negative electrodes in NIBs depend on the exposed NP surfaces, the (100) and (001) facets being much more effective than the most stable (101) surface. From an atomistic perspective, the behavior of these different surface terminations toward Na⁺ uptake remains unclear and there are still open questions about the Na⁺ storage mechanism. Actually, to the best of our knowledge, an in-depth understanding of Na-TiO₂ interactions is still missing and a conclusive theoretical interpretation of experimental evidences has not been provided yet. Different exposed surfaces in TiO_2 anatase NPs are suggested to act as Na^+ -insertion sites: beside the expected Na⁺ adsorption at NP surfaces, Na⁺ insertion would occur upon cycling, as a result of the pseudocapacitive behavior detected at the electrolyte/electrode interface. Attempts to explain the

anatase surface-dependent activities with just the surface adsorption fail in predicting the observed trend [70]. In particular, adsorption can only support the experimental evidence regarding the high activity of the (100) surface, but it does not explain the high performances of the NPs exposing the (001) surface. It means that Na coverage on the surface is not a complete nor reliable model for this electrode/electrolyte interface, where the charge and discharge involve also sodiation/desodiation processes, *i.e.*, insertion/deinsertion through the anatase NP lattice.

To address this knowledge gap, we have performed a first-principles study on $\mathrm{Na^{+}}$ adsorption and insertion at the (101), (100) and (001) $\mathrm{TiO_{2}}$ anatase surfaces. Structural and electronic features that drive the Na⁺-TiO₂ surface interaction are decoupled in order to prove the mechanism and the origin of the observed selectivity toward Na⁺ uptake. We have focused on the thermodynamically stable surfaces, *i.e.*, the (101), (100) and (001)low-index surfaces. TiO_2 anatase unit cell has tetragonal symmetry, belonging to the I_{41}/amd space group, and contains 4 formula units. We have obtained the PBE+U ground-state for TiO₂ bulk structure by relaxing both atom positions and cell volume. The theoretical lattice constants are in good agreement with experimental data at room temperature (a =3.839 Å and c = 9.843 Å show respectively 1.5% and 3.4% deviation from data reported in Ref. [72]). The PBE+U level of theory can provide higher accuracy compared to PBE functional in describing electronic features of the Na⁺ ion interacting with the transition metal-based oxide (see Section 5.1.1 for additional details). Comparable exposed surface areas can be obtained by cleaving up the bulk unit cell along the (101) direction, the $1 \times 2 \times 1$ supercell along the (100) and the $2 \times 2 \times 1$ along the (001). We have built three 6-layers slab models (24 f.u.-containing cells) by adding 10Å of vacuum along the *c* direction in order to avoid unfeasible interactions and carried out geometry optimization of slab models at PBE+U level of theory (see Figure 2.1). To avoid fictitious numerical effects, we have performed full relaxation of all the atoms in the surface slab models, thus obtaining surface energy values in agreement with literature [73].



Figure 2.1: PBE+U minimum-energy structures of **a**) (101), **b**) (100) and **c**) (001) TiO_2 anatase surfaces. Atoms are represented as spheres. Color code: Ti atoms in grey, O atoms in red.

Surface energy has been calculated according to Equation 2.1:

$$E_{surf} = \frac{E_{slab} - nE_{bulk}}{2S} \tag{2.1}$$

where E_{slab} and E_{bulk} are, respectively, the total energy of the optimized slab model and the bulk unit cell, n is the ratio between the number of formula units contained in the slab and that in the bulk unit cell, and Sis the exposed surface area. Table 2.1 collects all the related results.

Table 2.1: Lattice parameters, a and b (Å), exposed surface area, S (Å²), and surface energy, E_{surf} (J m⁻²) obtained from PBE+U minimum-energy structures. E_{surf}^{*} values from Ref. [73], are also reported for comparison.

(hkl)	а	b	\mathbf{S}	$\mathbf{E_{surf}}$	$\mathbf{E}^{*}_{\mathbf{surf}}$
(101)	10.566	7.678	81.127	0.613	0.49
(100)	9.843	7.678	75.582	0.715	0.58
(001)	7.678	7.678	58.957	1.087	0.98

The slab approach is the most commonly adopted method to model NPs. On one hand, crystal surfaces are dominant over the bulk state, due to the high surface/volume ratio in NPs. On the other hand, introducing vacuum space in the extended simulation cell largely reduces the computational cost and the reliability of the model compared to the cluster approaches. We have identified several Na adsorption and insertion sites as initial structures for our calculations. Insertion sites have been considered either in the subsurface layer (the first one underlying the surface layer) and in the following underlying one, along the [010] Na⁺ diffusion channel [68]. For adsorption sites lying on top of the clean surfaces, we have chosen specific configurations where Sodium could then insert into the TiO₂ lattice. All the explored configurations converged to a unique structure (see

discussion below). Electronic structure analysis confirms that our model consists of a Na⁺ cation interacting with a n-type semiconductor, *e.g.*, Na *s* states appear in TiO₂ conduction band (see Figure 2.3). We have calculated both Na adsorption and insertion energies for each surface as follows:

$$E_{ads} = E_{Na^{out}} - E_{slab} - \frac{1}{2}E_{Na}$$

$$E_{ins} = E_{Na^{in}} - E_{slab} - \frac{1}{2}E_{Na}$$
(2.2)

where $E_{Na_{out}}$ and $E_{Na_{in}}$ are the total energies of the optimized slabs with, respectively, one adsorbed and one inserted Na atom, E_{slab} is the total energy of the clean surface and E_{Na} is the total energy of Na metal (2atoms bcc cell), which is taken as reference [74]. In order to explain the different adsorption properties for each surface, we consider that part of the energy variation upon this process comes from the distortion energy, *i.e.*, the energy required to adapt the TiO₂ lattice in the pristine surface structure to the one in the Na-adsorbed state. We can define this quantity as:

$$E_{dist} = E_{slab}^{Na^{out}} - E_{slab}^{slab} \tag{2.3}$$

where $E_{slab}^{Na^{out}}$ and E_{slab}^{slab} are the energies of the slab at the geometry of Na adsorbed state and in its minimum-energy structure, respectively. Table 2.2 lists all the energy values computed for the different surface terminations.

Table 2.2: Adsorption, insertion and distortion energies, E_{ads} , E_{ins} and E_{dist} respectively, computed according to Equations 2.2 and 2.3. E_{ins} are compared to the TiO_2 anatase bulk value from Ref. [68]. All the values are expressed in eV and obtained at the PBE+U level of theory.

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	$\mathbf{E}_{\mathbf{ads}}$	$\mathbf{E_{ins}}$	$\mathbf{E_{dist}}$
bulk		0.531	
(101)	-1.120	0.266	0.577
(100)	-1.554	0.460	0.318
(001)	-0.801	0.364	0.726

Insertion energies are almost similar and close to the bulk reference value, while difference in adsorption energies are much more pronounced. From the results reported in Table 2.2, we can see that distortion effects clearly explain the adsorption trend. Also, the highly favorable Na adsorption on the (100) surface is supported by three extra Na-O interactions that are peculiar on this adsorption site, as shown in Figure 2.2. To the best of our knowledge, structural modifications (*e.g.*, phase transition) are likely to be less significant when anatase is synthesized in the form of NPs, due to the high surface/volume ratio of the NP allowing Sodium to intercalate at most to the subsurface layer, thus the full sodiation limit is not reached [75]. However, we have addressed eventual structural effects to the subsequent insertion of another Na⁺, which actually have not revealed any difference in adsorption and insertion properties. Electronic structure analysis has been performed in terms of charge density difference plots (CDs, Figure 2.2,

bottom panel) and PDOS (Figure 2.3) at the HSE06 level of theory (see Section 5.1.1 for further information on the use of hybrid functionals).



Figure 2.2: Top-view projection of the minimum-energy structures for Na adsorbed on the TiO_2 surface slabs with Na-O distances expressed in Å (top panel) and corresponding CD plots (bottom panel), isodensity value 0.004 a.u. Color code as in Figure 2.1, Na atom on (101), (100) and (001) surface is shown in blue, green and purple, respectively. Yellow and blue blobs represents electron accumulation and depletion, respectively. Na-O extra interactions are highlighted in (100) adsorption site (Na-O5 and Na-O6 are 3.51 Å and Na-O7 is 2.59 Å).

All the surface terminations show a common pattern. The adsorption of a Na atom leads to the reduction of Ti species and population of states



Figure 2.3: Atom- and angular momentum- PDOS for the a) (101), b) (100) and c) (001) TiO_2 surface slabs before (left panel) and after Na adsorption (right panel) at the HSE06 level of theory. Color code: Ti d states in black, O p states in red, Na s states in blue, green and purple respectively for (101), (100) and (001) surfaces.

at the edge of the TiO₂ conduction band, which is consistent with the desired n-type conductivity for the NIB electrode. At the same time, there is a consistent polarization of the oxygen species that are coordinating the adsorbed Na⁺ cation, determining the different relative stabilities of the resulting systems. Beside the adsorption process, Na⁺ ion insertion at the subsurface level is very likely to occur in TiO₂ anatase NPs. Thus, we have considered the minimum-energy structures of Na-adsorbed (Na^{out}) and Na-inserted (Na^{in}) systems as, respectively, the initial and final equilibrium states along the migration path. The process has been modeled by identifying three intermediate structures along the spatial coordinate from surface to subsurface positions. We have applied the CI-NEB [76] method to compute the MEP and the corresponding energetics (see Section 5.1.3 for further details on the use of CI-NEB method in VASP code). Top panel of Figure 2.4 shows the pictorial representation of the resulting MEPs for each surface.

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Figure 2.4: MEP (top panel) and corresponding energetics (bottom panel) for the Na migration through the a) (101), b) (100) and c) (001) surfaces. Energy barriers calculated from Equation 2.4 for the out/in migration are reported, respectively, to the left- and right-hand sides of the graph.

The process coordinate, ξ , is defined as the Na-Na distance between two contiguous points. The computed MEPs are identical in both forward and backward processes, *i.e.*, sodiation/desodiation. The anatase phase shows a 3D network formed by the stacking of zigzag chains, which consist of distorted edge-sharing TiO₆ octahedra. In this crystal framework, empty channels are possible interstitial sites for ion insertion and suitable-sized pathways for ion diffusion. As it can be observed in the top panel of Figure 2.4, Sodium moves along a given direction in the lattice, passes across the alternating Ti-O motif, that we have called "lattice window", and then enters the cavity in the subsurface layer. The cavity lies on the [010] diffusion channel. The energy barriers associated to both sodiation (out) and desodiation (in) processes can be determined as:

$$E_{migr}^{out} = E_{Na^{TS}} - E_{Na^{out}}$$

$$E_{migr}^{in} = E_{Na^{in}} - E_{Na^{TS}}$$
(2.4)

where $E_{Na^{out}}$, $E_{Na^{TS}}$ and $E_{Na^{in}}$ are the total energies of the initial, transition, and final states, respectively, along the MEP. Calculated E_{migr} for the out/in (sodiation/desodiation) process are showed in Figure 2.4 (bottom panel). The lowest energy barrier in both forward and backward directions is detected at the (001) surface, meaning that Na migration through (001) crystal facet is much more probable than in the case of (100) and (101) terminations. The positive values reported so far (insertion and migration energies) are consistent with the non-spontaneous sodiation of TiO₂ anatase NPs. Our model is a reliable representation of an anode interface that can be only sodiated upon charge (*i.e.*, provided an electrical potential is supplied). We aim to extend our model in the next future and include other elements that can possibly affect the migration energetics and thus the surface activity (*e.g.*, the electrolyte at the interface and the resulting passivating layer that can be formed, the external applied potential).



Figure 2.5: Top-view projection of the highest-energy structures along the migration path, Na^{TS} , for each surface (top panel) and the corresponding lattice windows (bottom panel). Color code as in Figure 2.2. Structural details of the lattice windows are reported in Table 2.3.

In order to rationalize the migration trend, we have focused on the structural modification of the different surface terminations upon Na migration. We have found that the size of the lattice window at the transition state (Na^{TS}) provides a direct measure of the steric hindrance that the migrating Sodium encounters along its path. As highlighted in Figure 2.5, the
lattice window is the area delimited by the Ti-O lattice and perpendicular to the path that Na⁺ should cross in order to enter the TiO₂ crystalline structure. The total area (A_{tot}) of the lattice window for each surface can be calculated straightforwardly from two Ti-Ti distances, a_1 and a_2 . However, this descriptor does not capture the significant difference between the lowest barrier found in (001) and the two higher ones in (100) and (101), as it can be seen from Table 2.3. Indeed, the limiting factor in the Sodium path is related to an effective lattice window, which is delimited by the shortest Ti-Ti distance, a_1 , thus defining the minimum accessible area, a_{min} .

Table 2.3: Total and minimum accessible areas, A_{tot} and a_{min} (Å²), of the lattice windows shown in Figure 2.5. Na^{out} refers to the minimum-energy structure of the adsorbed Na-ion (Figure 2.2) and Na^{TS} to the transition state structure (Figure 2.5). Migration energies, E_{migr} (eV), computed according to Equation 2.4 are also reported.

(hkl)	$\mathbf{A_{tot}}$		a_{min}		$\mathrm{E}^{\mathrm{out}}_{\mathrm{migr}}$
	Na^{out}	Na^{TS}	Na^{out}	Na^{TS}	
(101)	11.4	12.3	8.7	9.6	2.641
(100)	11.4	12.6	8.7	9.9	2.814
(001)	15.2	14.9	15.1	14.8	1.463

This descriptor inversely correlates to the barrier heights calculated for the different surfaces: smaller lattice windows in (101) and (100) surfaces result in higher barriers, while the (001) surface shows the largest lattice window and, thus, the lowest barrier. From our DFT investigations, we can conclude that:

- the most favorable adsorption for Na^+ is found at the (100) termination of TiO₂ anatase, thanks to a convenient accommodation of the large cation on a surface step that maximizes the Na^+-O^{2-} interactions and does not perturb much the crystalline lattice;
- the charge/discharge processes in TiO_2 anatase NPs can effectively occur via Na insertion mechanism. We have proven that the (001) surface is the most active toward Na subsurface insertion thanks to its peculiar structural features: the large surface lattice window allows for an easy diffusion of the large Na⁺. This finding supports the experimental observation of high-performing TiO₂ NPs exposing the (001) surface termination;
- analysis of MEPs in all the surface terminations demonstrates that the corresponding migration barrier heights depend only on structural modification of the anatase lattice upon Na⁺ insertion, thus unveiling the key role of surface lattice windows.

The identification of this easy computable structural descriptor can be very useful to design and develop new high-performing materials with potential efficient Na uptake mechanism. All the results reported in this section have been published as an open-access paper in the peer-reviewed journal *Nanoscale Advances* in 2020 [77].

2.2 $MoS_2/Graphene$ heterojunction: an example of 2D electrode

Since discovery of Graphene, 2D-materials have become the focus of intense research for several applications in catalysis, electronics and optoelectronics [78–80]. In the last decade, efficient and low-cost synthetic strategies for large-scale production have been developed, including mechanical or chemical exfoliation into single or few layers [81, 82]. Transition metal dichalcogenides (TMDCs) have attracted significant attention owing to outstanding properties and natural abundance. Molybdenum disulphide (MoS_2) has been widely studied as largely flexible material, highly performing catalyst toward hydrogen evolution reaction (HER) and promising negative electrode in lithium ion batteries (LIBs) [83–86]. More recently, the favorable intercalation structure for Na ions has paved the route toward the use of MoS_2 as anode material in Na-ion batteries (NIBs) [3]. The large Na⁺ radius hinders a convenient reversible storage into the structure of common negative electrodes (e.g., graphite or Silicon). TMDCs seem to be well-suited to this end, thanks to the tunable dimensions of interlayer spacing and to the precise nanostructuring that would lead to enhanced ion/electron diffusion kinetics and thus to improved efficiency. Despite showing high theoretical reversible capacity, MoS₂ suffers of low electronic conductivity and huge volume variation during sodiation/desodiation processes, leading to quick capacity fading. Combination with carbon matrices

has emerged as a promising solution [30, 87]. The disordered microstructure of HC can provide porous surface area suitable to accommodate active material NPs [88], but safety concerns related to electrodeposition of Na metal can limit its applicability [89]. Soft carbon shows a graphite-like layered structure that would be appropriate for Na⁺ uptake and storage, but the mass loading is generally low due to the limited surface area [90]. Lately, the use of Graphene has also been considered to enhance electrical conductivity with no need of further additives, improve the mechanical robustness with volume expansion upon cycling being largely restrained, and boost the rate capability and the cycle stability owing to the nanostructured matrix [91-93]. Producing hybrid MoS₂/Graphene based anode materials has therefore appeared as a promising option. Both composite [94, 95] and monolayered [96, 97] MoS₂/Graphene electrodes have been produced via easy and low-cost procedures, leading to high-quality and efficient materials (*i.e.*, stable charge capacity, high coulombic efficiency). Exfoliation of MoS_2 can lead to specific monolayered structures differing for coordination and electronic properties. The MoS_2 structure consists of MoS_6 units sharing two S atoms that can display different intra- and inter-layer symmetries: the two thermodynamically stable phases, 2H and 3R, show D_{3h} point group symmetry around Mo centre but different space groups $(P6_3/mmc \text{ and } R3m, \text{ respectively})$ and are semiconductors [98]; the metallic 1T-phase shows O_h point group symmetry around Mo centre and belongs to P-3m1 space group [99]. It should be highlighted that

2H- and 3R-phases are identical in the monolayered structure. While controlled synthesis of monolayered 2H-MoS₂ has been well established (large surface area, high quality, number of layers, vertical and in-plane heterostructures), less is known about direct growth of $1T-MoS_2$ because of the intrinsic instability [100, 101]. Despite the majority of studies has been dedicated to $2H-MoS_2/Graphene$ electrodes [94–97, 102–105], there is an increasing interest for the 1T-counterpart. Exfoliation synthesis assisted by alkali ion intercalation can lead to highly pure products [106, 107]. 1T-based films also seem to limit the capacity fading when tested in both LIBs and NIBs compared to 2H-counterpart [108, 109]. Understanding the subtle structure-property relationship underlying $MoS_2/$ Graphene-based materials is key to boost their application in advanced functional NIB devices [105]. The interest in studying heterojunction has extremely grown in many research fields from both the theoretical [110-121] and the experimental [122–124] points of view, since the properties of hybrid interfaces are not necessarily given by the sum of the single components.

In this context, we have carried out a DFT-D study on $2D-MoS_2/Graphene heterostructure and focused on the role of <math>MoS_2$ phase in determining the activity toward Na⁺ uptake and diffusion. Details on the use of *a posteriori* correction to include dispersion contribution to the DFT energy can be found in Section 5.1.2 of this Thesis. We aim at dissecting the structural and electronic features of $MoS_2/Graphene$ interface upon Na intercalation and migration. As the monolayered 2H- and 3R-structures are identical, we have only considered 1T- and 3R-phases and performed the geometry

optimization of their bulk states at the PBE-D3BJ level of theory (see Figure 2.6 and Table 2.4).



Figure 2.6: Minimum-energy structures of MoS_2 obtained at PBE-D3BJ level of theory and structural details showing the punctual symmetry on the Mo coordination centre: **a**) 1T phase, O_h point group; **b**) 3R phase, D_{3h} point group. Color code: Mo atoms in violet, S atoms in yellow. Structural parameters are reported in Table 2.4.

The lattice constants are in good agreement with experimental data, showing the maximum deviation of 0.43% on the *c* value in the 3R phase. We have cleaved the equilibrium bulk structures to obtain single layers of 1Tand 3R-MoS₂. While the monolayered (ML) structure of 3R is retained, 1T-ML undergoes structural distortion and stabilizes in a different geometry, namely 1T' phase (Figure 2.7a), as reported in the literature [125]. It is noteworthy that the distorted phase looses the metallic character, as shown in Figure 2.7b. For sake of simplicity, from this point forward we are going to refer to this distorted 1T' phase as 1T-MoS₂.

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Table 2.4: Lattice parameters, a, c (Å) and γ (°), of PBE-D3BJ minimumenergy structures shown in Figure 2.6. Experimental values from Refs. [126, 127] are reported for comparison.

phase	\mathbf{method}	а	с	γ
$1\mathrm{T}$	this work	3.180	5.920	120
	exp^*	3.190	5.940	120
3R	this work	3.150	18.290	120
	exp^*	3.160	18.370	120



Figure 2.7: a) Energy scan of the lattice constant for 1T-ML computed at the PBE-D3BJ level of theory. Green circle indicates the value of groundstate bulk structure (a = 9.526 Å), while red circle the equilibrium value of the ML geometry (a = 9.602 Å). Inset: structural details of 1T and 1T'. b) Atom- and angular momentum- PDOS computed at the PBE-D3BJ level of theory for 1T- and 1T'-ML structures. Color code: Mo d states in violet, S p states in yellow.

To combine the 1T- and $3R-MoS_2$ monolayers with Graphene, we have built up $3\times3-MoS_2$ and 4×4 -Graphene supercells in order to match the periodicity of both crystalline lattices. The two layers have been placed at a distance of 3.5 Å, and 15 Å of vacuum have been added along the *c*direction to model a 2D-structure. The final slab model contains 9 formula units of MoS_2 for both phases and 32 Graphene carbon atoms. Figure 2.8a shows the energy scan of the lattice constant that has been performed to get the equilibrium geometries. The so-obtained structures and corresponding parameters are reported in Figure 2.8b and Table 2.5, respectively.



Figure 2.8: a) Energy scan of the lattice constant for 1T- and 3R-MoS₂/G 2D-heterostructures. Red circles highlight the obtained equilibrium values, a = 9.810 Å and 9.758 Å for 1T- and 3R-MoS₂/G, respectively. b) Side and top views of minimum-energy structures for 1T-MoS₂/G and 3R-MoS₂/G obtained at the PBE-D3BJ level of theory. Color code as in Figure 2.6, C atoms in grey. Structural parameters are reported in Table 2.5.

We understand that this kind of materials can show multitudinous structures. Several works have addressed the properties of $MoS_2/Graphene$ interfaces to the stacking configurations and it seems that S-C coordination does not affect the adsorption of Graphene on MoS_2 monolayers (similar binding energies, corrugation of Graphene) [116]. However, Hieu and co-workers have reported a slightly more stable configuration with larger interlayer spacing [111]. Our choice for the $MoS_2/Graphene$ configuration is based on this consideration, taking into account the stacking arrangement with larger interlayer spacing as a representative structure to model Na intercalation and diffusion. After geometry optimization, the interlayer distance (which is taken as the smallest S-C distance) results to be 3.11 Å and 3.35 Å for 1T- and 3R-MoS₂/G, respectively. These values cover the typical range of vdW-based interactions, which endorses our choice to take into account dispersion forces, and still seem to be suited for ion intercalation. For both phases, the lattice constant of the heterostructure is closer to Graphene rather than to MoS_2 (see Figure 2.8a). This can be related to the stiffness of the two materials, with the more flexible MoS_2 undergoing the greater structural variation. The strain that the two materials experience when faced to each other can be quantified in terms of the lattice mismatch, which is defined in Equation 2.5:

$$\varepsilon\% = \left(\frac{a^{hybrid}}{a^{pristine}} - 1\right) \times 100 \tag{2.5}$$

where $a^{pristine}$ is the lattice constant of 2D-MoS₂ and Graphene at their

equilibrium geometries and a^{hybrid} is the lattice constant of the heterostructure. By looking at Table 2.5, we can see that the MoS₂ stretching and the Graphene compression are represented by, respectively, positive and negative values of ε . The higher absolute values of ε (MoS₂) account for the larger flexibility of Molybdenum disulphide compared to Graphene. The thermodynamic stability of such hybrid materials can be described in terms of binding and adhesion energies. The former is defined as the energy required to form the heterostructure from the pristine materials, while the latter represents the energy exchanged when the two layers are faced to each other:

$$E_{bind} = E_{MoS_2/G} - E_{MoS_2} - E_G$$

$$E_{adh} = E_{MoS_2/G}^{MoS_2/G} - E_{MoS_2}^{MoS_2/G} - E_G^{MoS_2/G}$$
(2.6)

 $E_{\text{MoS}_2/G}$, E_{MoS_2} and E_G are the total energies of, respectively, the hybrid, pristine MoS₂ and Graphene systems, $E_{\text{MoS}_2}^{\text{MoS}_2/G}$ and $E_G^{\text{MoS}_2/G}$ are the total energies of the pristine materials at the geometry of the heterostructure.

Table 2.5: Lattice constant and interlayer distance, a and d (Å), lattice mismatch, ε , binding and adhesion energy, E_{bind} and E_{adh} (eV), calculated according to Equation 2.6 for both 1T- and 3R-MoS₂/G heterostructures.

phase	a	d	$\varepsilon/{ m MoS_2}$	$arepsilon/{f G}$	$\mathbf{E}_{\mathbf{bind}}$	$\mathbf{E}_{\mathbf{adh}}$
$1 \mathrm{T-MoS}_2/\mathrm{G}$	9.810	3.110	2.17%	-0.71%	-0.665	-1.649
3 R-MoS $_2/G$	9.758	3.350	3.26%	-1.25%	-0.026	-1.653

 $1T-MoS_2/G$ system shows more negative binding energy compared to 3R- MoS_2/G , which can be related to the smaller lattice mismatch. In fact, since adhesion contribution is the same, the difference in binding energy arises from barely distortion effects (E_{dist} (3R-MoS_2/G) 1.627 eV $> E_{dist}$ (1T-MoS $_2/{\rm G})$ 0.984 eV). This result is not surprising, and it has been observed for different kind of materials that a certain amount of energy is required to allow structural rearrangements, *i.e.*, distortion energies are usually positive [77, 128, 129]. Formation of $1T-MoS_2/G$ is expected to be thermodynamically easier due to the minor strain experienced by both $1T-MoS_2$ and Graphene. On the other hand, adhesion energies are rather similar, which would suggest that the electronic interaction with Graphene is not affected by MoS_2 phase. Overall energy variations are negative and no Graphene distortion is observed, showing that both phases of $2D-MoS_2$ are predicted to form thermodynamically stable heterostructures with Graphene without affecting its structural properties. Electronic structure analysis has been performed in terms of band structure, PDOS and CD plot at the PBE-D3BJ level of theory (Figure 2.9). The band structures are calculated self-consistently at the PBE-D3BJ level of theory along the Γ -K-M- Γ direction in reciprocal space by considering 10 k-points divisions along each segment [130]. Our calculations show that both heterostructures are electronically conductive and that a charge transfer occurs from Graphene to MoS_2 . In $3R-MoS_2/G$, the MoS_2 band gap is filled by the Graphene states, with a shift of the Dirac cone to higher energy states resulting in a p-type contact and a shift of the MoS_2 Conduction Band Minimum (CBM) from K to Γ point [120, 131, 132]. Conversely in 1T-MoS₂/G, both MoS₂ and Graphene participate to electron conduction, but the same p-type effect is found also in this case. The shift of the Dirac cone in the Graphene band structure is commonly related to the presence of an electric field (*e.g.*, electron doping or applied external bias) [117, 118, 121], but it has been observed also when Graphene is faced with WS₂ [113] or with a single layer of MoS₂ upon induced-strain [120].



Figure 2.9: Electronic structure analysis computed at the PBE-D3BJ level of theory: (from left to right) band structure, atom- and angular momentum- PDOS, CD plot of 1T-MoS₂/G and 3R-MoS₂/G heterostructures (isosurface level: 0.27 meV Å^{-3}). Color code as in Figures 2.8 and 2.7, green and blue blobs represent electron accumulation and depletion, respectively.

These findings point out the importance of considering both mechanical

and electronic coupling when dealing with vdW heterostructures [123, 124]. According to several recent works, the lattice strain also seems to play a role in shifting the MoS_2 CBM from K to Γ point [120, 131, 132]. However, we know that this kind of features in band structures could also arise from the band folding effect occurring when larger cells are considered. In our case, the choice of the supercell dimension is motivated by the need to consider the smallest cell for the demanding computation of Na intercalation and migration. To the best of our knowledge, there is an open debate in the literature concerning the opening of a band gap in the Graphene band structure [111, 119]. Whether this is due to structural (e.g., strain, stacking) or electronic (e.g., electric field, electron doping) reasons is still unclear, however the band gap is rather small and does not jeopardize the electron conduction in $MoS_2/Graphene$ interfaces observed experimentally. Comparison with electronic structures of the single components clearly shows that the role of the interface is crucial: the freestanding $1T-MoS_2$ monolayer, in its more stable distorted structure, shows a small band gap, losing the metallic character typical of the bulk state (Figure 2.7b), while the direct band gap of $3R-MoS_2$ monolayer is centered on the K point. These significant variations corroborate the importance to focus on heterostructures and not just the pristine materials. Regarding CD plots, the electron depletion at Graphene side (blue blobs) leading to electron accumulation at MoS_2 one (green blobs) mainly involves C and S p states, with a minor contribution of Mo d states in the 1T-case. This

charge transfer also reflects in the band structures where the p-doping experienced by Graphene results in the upwards shift of the Dirac cone, as discussed above. From this analysis, we would expect that MoS_2 is going to play an active role upon Na⁺ intercalation since it is the one gathering the electronic charge. Na intercalation at the MoS_2/G interface is modeled by considering a Na atom placed within the interlayer spacing in the (4×4) Graphene/(3×3) MoS₂ supercell. Because of the uneven correspondence between atomic sites in both parts of the hybrid system, several intercalation sites can exist with different Na coordination to each material. We have computed the PDF of Na-Mo, Na-S, and Na-C distances (Figure 2.10) to rationalize all intercalations sites. For the 1T-polymorph, two kinds of coordination sites involve Na and MoS_2 : (1) those where Na is coordinated to four S atoms with distances around 2.5 Å and to three Mo atoms at ~ 3.5 Å labeled as hollow sites and (2) those with a similar Na-S coordination but a peak on the Na-Mo PDF at ~ 3 Å, indicating the coordination to one Mo atom and labeled as top sites. Considering coordination of Na with Graphene, we can distinguish (1) edge and (2) hollow sites, which differ only in the less intense peaks at ~ 2.5 Å for the edge, since Na is coordinated to only two C atoms compared to the six ones for the hollow. From the combination of the two different coordination modes to MoS_2 (hollow or top) from one side and the other two modes to Graphene on the other side (edge or hollow), all Na sites can be classified into four possible groups (Figure 2.10a). Also, four coordination sites and similar observations can be identified for $3R-MoS_2/G$ (Figure 2.10b), except that the Na-S coordination involves three S atoms instead of four. In general, the PDFs computed for the 3R-phase show narrower and more defined peaks, which is representative of a more ordered structure. We have calculated the Na intercalation energy according to Equation 2.7 for each explored configuration:

$$E_{int} = E_{Na@host} - E_{host} - \frac{1}{2}E_{Na}$$
(2.7)

where $E_{Na@host}$ and E_{host} are the total energies of Na-intercalated systems and the host materials, respectively, and E_{Na} is the total energy of Na metal in the body-centered cubic (bcc) structure (which contains 2 atoms per cell) computed at the same level of theory [74, 133]. The results are listed in Table 2.6.

Table 2.6: Sodium intercalation energies, E_{int} , at different intercalation sites described in Figures 2.10a and 2.10b, calculated according to Equation 2.7. All the values are expressed in eV.

phase	top-hollow	hollow-hollow	$\mathbf{top}\operatorname{-edge}$	hollow-edge
$1\mathrm{T}\text{-}\mathrm{MoS}_2/\mathrm{G}$	-1.222	-0.914	-1.105	-1.150
3 R-MoS $_2/G$	-0.162	0.131	-0.089	-0.065

The overall intercalation energies are negative, suggesting that the formation of Na-intercalated compounds would be favorable for both phases.



Figure 2.10: PDF of Na-Mo (purple), Na-S (yellow) and Na-C (grey) distances computed for the four possible intercalation sites at **a**) 1T-MoS₂/G and **b**) 3R-MoS₂/G. Color code as in Figure 2.8, Na atoms in red. Corresponding structural details are shown to the side.

However, 1T-phase seems to be more active toward Na intercalation showing more negative E_{int} values, which would explain the experimental evidence of phase stability variation upon ion intercalation [106, 107]. Electronic structure analysis on Na-intercalated compounds can clarify to what



extent Na intercalation modifies the electronic structure at the interface.

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Figure 2.11: Electronic structure analysis computed at the PBE-D3BJ level of theory: (from left to right) band structure, atom- and angular momentum- PDOS, CD plot of Na-intercalated compounds in both 1T- MoS_2/G and $3R-MoS_2/G$ (isosurface level: 2 meV Å^{-3}). Color code as in Figures 2.9 and 2.10.

Bader charge analysis reveals that the formal charge carried by Na is +0.84in both 1T- and 3R-MoS₂/Graphene, thus indicating that our model is reliable for a Na⁺/electrode system. In Figure 2.11, we have reported band structures, PDOS and CD plots computed at the PBE-D3BJ level of theory for the most stable systems. Both band structures (left panel in Figure 2.11) show the CBM of MoS₂ crossing the Fermi level, which is consistent with the desired n-type conductivity for the NIB electrode. CD plots (Figure 2.11, right panel) display a consistent polarization of the

S and C atoms that are coordinating the Na cation. However, the excess electronic charge seems to transfer from Na to MoS_2 side, where the electron density delocalizes along the entire layer. The possible migration paths and the corresponding energetics have been explored to understand how the structural and electronic features of these heterointerfaces can affect the diffusion of the Na ion. The mechanism of Na migration through MoS_2/G interface has been derived from first principles by means of CI-NEB method [76] (see Section 5.1.3 for further details). We have identified two different pathways for each heterostructure, labelled as path A and B. In each path, Na can move along the x direction, where the S atoms pointing toward the interlayer spacing seem to create a proper diffusion channel (Figure 2.12a, top). We have considered all the intercalation sites lying on a given channel and applied the CI-NEB method to determine the MEP for Na migration (Figure 2.12a, bottom). To describe the whole migration mechanism, closed pathways have been selected, with the final structure being the image of the initial one. Figure 2.12b shows the resulting energetics as function of the migration coordinate (ξ , Na-Na distance after each Na jump). In $3R-MoS_2/G$, paths A and B (dashed and solid lines, respectively) result to be almost similar, with all the intermediate structures lying very close in energy. All the barriers associated to the Na jump are in the range 0.17-0.22 eV. Contrarily, migration through the $1T-MoS_2/G$ interface is much less regular for both pathways, with larger energy differences among the explored sites. Path A (dashed lines) shows migration barriers going from ~ 0.08 to ~ 0.70 eV, while ~ 0.34 and ~ 0.59 eV values are found for path B (solid lines).



Figure 2.12: a) Side and top views of Na migration pathways through 1T-MoS₂/G and 3R-MoS₂/G; b) corresponding energetics computed with CI-NEB method at the PBE-D3BJ level of theory. Color code as in Figure 2.10.

These values can be compared to Na diffusion barriers obtained with similar approaches for MoS_2 bulk (~0.7 eV) [102], freestanding MoS_2 [103] and Graphene sheets (~0.3 and ~0.1 eV, respectively) [134], and also evaluated as function of MoS_2 interlayer spacing (from 1.2 to 0.2 eV at increasing spacing) [104]. In general, Na mobility seems to be enhanced when moving from bulk to 2D-like structures. Our computed barrier heights are also directly comparable to those reported by Sun and co-workers on top of

Graphene-supported MoS_2 monolayers (from 0.07 to 1.09 eV) [96]: while in the work by Sun *et al.* Na diffusion barriers go up to ~ 1.1 eV in certain directions, in our case the highest barriers are 0.70 eV for 1T- and 0.25 eV for $3R-MoS_2/G$, indicating that the interlayer diffusion can be more convenient for Na mobility. So as to explain the different behavior among our explored pathways, we have focused on the structural features of such intermediates along the migration coordinate. By looking at the local coordination of the migrating Na⁺, we have found that the single jump is more likely to occur (*i.e.*, shows a lower energy barrier) when Na is further from the S atoms (as a matter of fact, the hypothetical top-S intercalation site does not represent a stable configuration). To visualize to what extent the S coordination around Na changes when the highest transition state is reached, we have computed the Na-S PDFs at the minimum- and highestenergy structures for A and B migration paths (as shown in orange and red colors in Figure 2.13, respectively). Migration barriers generally arise from the shortening of two Na-S distances below the equilibrium value, as suggested by the left-shift of the red peaks around 2.5 Å. In particular, this is more relevant in the case of $1T-MoS_2/G$ (top panels of Figure 2.13), where the Na-S distance becomes even shorter and leads to E_{migr} equals to 0.696 eV and 0.586 eV for paths A and B, respectively. It is noteworthy that the interlayer spacing increases upon Na intercalation and migration, with major distortion associated to 1T rather than 3R-case (the former showing d values increasing from 3.11 Å to 3.70 Å when going from the minimum to the highest-energy structure along the migration coordinate,



while the latter from 3.35 Å to 3.76 Å).

Figure 2.13: PDF of Na-S distances at the highest (red) and minimumenergy structures (orange) along the migration pathways reported in Figure 2.12. Inset: pictorial top-view representations of the short-range Na-S coordination. Color code as in Figure 2.10, Na atoms at the highest- and minimum-energy structure in red and orange, respectively. Only S atoms from MoS_2 are shown for clarity.

From these results, $3R-MoS_2/G$ is predicted to allow an easier Na diffusion through the interface compared to its 1T-counterpart. However, considering the more favorable intercalation energies of the 1T-MoS₂/G heterostructure, we think that some strategies (*e.g.*, Sulphur vacancies, grain boundaries and/or defect engineering) aiming to lower the migration barrier at this interface should be developed in order to boost its application as promising NIB electrode. In conclusion, our study has shown that:

- both single layers of 1T- and 3R-MoS₂ can be combined to Graphene into thermodynamically stable 2D hybrid materials, as suggested by the favorable binding and adhesion energies. The smaller lattice mismatch for the 1T-MoS₂ accounts for the slightly more favorable binding of this phase to the Graphene sheet. Both heterostructures show a moderate charge transfer occurring from Graphene to MoS₂ layer and a metallic character in their band structures, thus proving that interfacial effects can completely modify the properties of pristine materials (both 3R- and distorted 1T-monolayers have band gaps);
- MoS₂/Graphene can form stable Na-intercalated compounds in both phases, with 1T showing more favorable intercalation energies than 3R. This agrees with 1T-MoS₂ becoming more stable in the presence of intercalating alkali ions. MoS₂ turns out to be the active material upon Na intercalation since it is the one gaining the electronic charge from Na cation, as shown by the CD plots;
- Na⁺ can easily migrate along the direction parallel to the hybrid interface. Analysis of the diffusion mechanism shows that Na migration

could be hindered by S atoms pointing towards the interlayer spacing, thus leading to higher migration barriers in $1T-MoS_2/G$ when Na-S distances along the path become too small. Several strategies, such as introducing S vacancies, can be developed in order to improve Na mobility at this hybrid interface.

Our results and the new insights at the atomistic level can be useful to experimental efforts toward the development and optimization of 2D hybrid materials for applications in NIBs. In the next future, we aim at unveiling the role that defect chemistry and morphology can play in determining the activity of MoS_2/G -based electrode materials. These preliminary outcomes have been published in an open-access article on the *Journal of Physical Chemistry C* in 2021 [135].

3 Charge compensation mechanisms in high-energy cathodes

Development of high-energy and structurally stable NIB positive electrodes operating at voltage values in the order of 4.5 V (or even above) represents a current Grand Challenge because it is the cathode that mainly affects the battery performance and manufacturing costs. Among several explored materials, layered transition metal (TM) oxides, Na_xTMO₂ (0 < x < 1), have attracted special attention thanks to their easy synthesis and promising electrochemical performances [136–140]. Similar to Li_xTMO₂ counterpart, the crystalline structure alternates planar layers of edge-sharing TMO₆ octahedra and alkali metal ions, where Na ions can easily move in and out upon cycling, with the charge being compensated by the reversible reduction and oxidation of TM ions. Na_xTMO₂ can crystallize in either O3 or P2-polymorphs, which differ in the symmetry at the Na site (octahedral O or prismatic P) and the number of TMO₂-layers in the unit cell (3 layers with "ABC" scheme for Oxygen stacking in the O3

packing, or 2 layers with "ABBA" sequence in the P2 one) [141]. P2-type phases usually exhibit excellent reversible capacity and superior rate perfor mance compared to O3 ones, thanks to a higher Na^+ mobility enabled by the open prismatic diffusion pathways and higher Na content, which allows larger specific capacity and improved stability [142–144]. However, a simple gliding of TMO_2 sheets with no breaking of M-O bonds can occur upon electrochemical cycling, leading to an undesired P2-O2 phase transitions and related instability issues [145, 146]. For certain compositions, for example Fe-containing TMO₂, even very complex P2-O2 phase transitions have been reported at high operating voltage, involving dynamically changing inter-growth structures called "Z"-phase [147, 148]. Among all TMs layered oxides, many studies focus on Mn because it promises reduced costs, increased sustainability and improved performance [149]. In what follows, we extensively discuss our *ab initio* investigation on a layered Mn-deficient oxide, $Na_x Ni_{0.25} Mn_{0.68} O_2$, that has shown encouraging performances in NIBs but still peculiar electrochemical features need to be enlightened.

3.1 Anionic redox activity: $Na_x Ni_{0.25} Mn_{0.68} O_2$ as case study

One of the main issues when employing P2-type layered Na_xMnO_2 oxides as positive electrodes in NIBs is to retain the P2 structure upon cycling. A widely exploited approach consists in playing ion substitutions at the Mn site by metal doping (e.g., Li⁺, Mg²⁺, Ti⁴⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, $\mathrm{Zn}^{2+}),$ which can sensibly affect the phase stability [50, 140, 147, 150– 156]. Also, it has been shown that the substitution of inert alkali metals, such as potassium, at the Na site in $Na_x TMO_2$ allows to uphold the layer-structured framework upon cycling [139]. Remarkably, recent works have suggested that high energy density in both LIBs and NIBs can be attained via an additional redox activity, *i.e.*, the charge being stored not only by the TM but also by the oxide sublattice [139, 157-161]. In this way, the theoretical specific capacity goes beyond the fixed limits of TM redox potentials, leading to a new paradigm in research and development of advanced cathode materials. Experimental evidence of Oxygen participation to charge compensation upon delithiation is extensively reported [162–167], and its correlation with high Li content elucidated from *ab ini*tio calculations [168]: in alkali-rich layered oxides, some Oxygen atoms are coordinated by two TMs, thus showing a nonbonding 2p Oxygen orbital just below the Fermi level, which can directly participate in the oxidation process. These findings have suggested an optimization strategy based on alkali metal ion substitutions at the TM Wyckoff sites, but it has been observed that the metal migrates upon cycling, with detrimental effects on overall performances [169, 170]. Introducing a TM vacancy has emerged as another possible approach, leading to similar 2p nonbonding orbital on Oxygen atoms and, at the same time, keeping the TM migration suppressed [144, 171]. Whether these materials can accomplish a fully

reversible O-redox process or undergo O_2 loss still remains an open question [144, 172]. Recently, the first-cycle voltage hysteresis observed during galvanostatic cycling of Na-based high-energy cathodes has been associated to cation ordering at the superstructure level, suggesting that specific arrangements can drive the stabilization of Oxygen electron holes and preserve the O-redox activity upon subsequent cycling [157, 173]. However, an in-depth investigation on these charge compensation mechanisms is still missing. Indeed, increasing efforts are devoted to assess the structureproperty-function relationships in these promising NIB electrode materials and to find suitable descriptors able to correlate their chemical compositions and electrochemical performances [174]. Computational modeling offers the atomistic perspective needed to elucidate the details of Oxygen redox and the effects of point defects on the related mechanisms. The success of *in silico* experiments is well-established in this research area as rational strategies are fundamental toward the design of highly performing Sodium intercalation electrodes for advanced Na-ion batteries [74, 175, 176].

Within this context, we have performed a first-principles study of the P2type Mn-deficient layered oxide $Na_xNi_{0.25}Mn_{0.68}O_2$ (NNMO). This material exhibits outstanding electrochemical performance for rechargeable NIBs [144]. From EELS and sXAS experiments, the electrochemically cycled NNMO particles show a gradient of TM oxidation states that is ascribed to the loss of Oxygen [144]. Our aim is to dissect this NNMO feature at the atomistic level and from first principles, so to determine the O-redox activity at different sodiation stages, while concurrently providing new insights on the underlying mechanisms. We have built up a $4\times4\times1$ supercell of the stoichiometric Na_xNi_{0.25}Mn_{0.75}O₂ structure and applied the special quasi-random structure (SQS) method in order to get a random distribution at Ni/Mn sites [177, 178]. The SQS is a state-of-the-art method to study solid solutions with two or more components [179–182], and would allow our NNMO local minimum-energy structures to account for the configurational entropy properly. Na atoms have been placed in edge (e) and face (f) sites so that the e/f ratio would be equal to 2 [183], this occupation being kept constant within the single layer. Lattice constants and atomic positions for the Na_xNi_{0.25}Mn_{0.75}O₂ system with x =0.125, 0.25, 0.50, 0.75 have been fully relaxed (see Table 3.1).

Table 3.1: Lattice parameters, a and c (Å), of $4 \times 4 \times 1$ Na_xNi_{0.25}Mn_{0.75}O₂ supercells (x = 0.75, 0.50, 0.25, 0.125) computed at the PBE+U(-D3BJ) level of theory. Experimental values from Ref. [144] are shown for comparison.

x Na		a	С		
	this work exp^*		this work	exp^*	
0.75	11.658	2.880 (11.520)	11.423	11.128	
0.50	11.579	2.863 (11.452)	11.346	-	
0.25	11.514	-	11.283	14.021	
0.125	11.500	2.858 (11.432)	11.269	14.224	



Figure 3.1: a) Representation of Mn sites where the vacancies have been introduced. Oxygen atoms have been removed for clarity. Atoms are depicted as spheres. Color code: Na in yellow, Ni in green, Mn in purple, Mn atoms to be removed in pink. b) PDF of Na-O distances in stoichiometric $(Na_x Ni_{0.25} Mn_{0.75} O_2)$ and Mn-deficient $(Na_x Ni_{0.25} Mn_{0.68} O_2)$ phases computed at the PBE+U(-D3BJ) level of theory at each sodiation state.

The deviation from experimental values is lower than 2% on the *a* lattice constant at each sodiation state. The higher deviation on the *c* values, the experimental ones being larger, is due to intercalation of solvent molecules as suggested in Ref. [144]. We have focused on the Mn-deficient $Na_x Ni_{0.25} Mn_{0.68} O_2$ phase as the presence of Mn vacancies is shown to be beneficial for the cathode performances and is considered responsible for the O-redox activation [144]. We have introduced two Mn vacancies arranged in the most homogeneous configuration (shown in Figure 3.1a) and performed the optimization of atomic positions since no significant variation of lattice constants was assumed. Figure 3.1b compares the relative Na occupancy at edge/face (e/f) sites between the stoichiometric and the Mn-deficient phases in terms of PDF of Na-O distances. It can be observed that face sites in NNMO are stabilized over the edge ones, compared to the stoichiometric counterpart. In particular, the e/f values turn out to be lower than 2, as also reported in Figure 3.2a. For the ground-state NNMO structures obtained at the PBE+U(-D3BJ) level of theory (Figure 3.2a), we have calculated the intercalation potential values for each sodiation stage according to Equation 3.1:

$$V = -\frac{(E_{Na_{x_2}} - E_{Na_{x_1}} - (x_2 - x_1)\frac{1}{2}E_{Na})}{(x_2 - x_1)}$$
(3.1)

where $E_{Na_{x_2}}$ and $E_{Na_{x_1}}$ are the total energies of NNMO at, respectively, x_2 and x_1 Na composition ($x_1 < x_2$), E_{Na} is the total energy of Sodium metal considering the bcc lattice with 2 atoms in the unit cell [74]. The corresponding computed capacity-voltage profile (red profile in Figure 3.2c) is in qualitative agreement with intercalation potentials derived from the available experimental data (blue profile in Figure 3.2c), thus confirming the reliability of our model [144]. We have analyzed the structural properties along the desodiation process by calculating the PDF of Mn-O and Ni-O distances, as shown in Figure 3.2d. While Mn-O distance pattern is almost identical for each sodiation degree (with an average value of ~1.9Å), Ni-O bonds undergo a significant shortening with decreasing Na content (the highest peak shifting from ~2.1Å to ~1.8Å). Analysis of the electronic structure clarifies the origin of these structural features. The magnetization of each Mn and Ni atom, plotted against Na content (Figure 3.3 a and b, respectively), reveals that desodiation induces $Ni^{2+} \rightarrow Ni^{3+}$ and then $\rightarrow Ni^{4+}$ oxidation, while Mn^{4+} oxidation state is essentially retained.



Figure 3.2: a) Minimum-energy structures of NNMO systems obtained at the PBE+U(-D3BJ) level of theory. Coordination octahedra at the TM (TM = Mn, Ni) sites are highlighted. Color code as in Figure 3.1, O in red. Values of e/f ratio after relaxation are reported. b) Coordination details of both edge and face Na sites. c) Computed capacity-voltage plot of NNMO (red solid lines) in comparison to experimental-derived data taken from Ref. [144] (blue dashed lines). d) PDF of Mn-O (purple) and Ni-O (green) distances in NNMO computed at the PBE+U(-D3BJ) level of theory.

This is in agreement with previous spectroscopic measurements performed on similar $Na_xNi_yMn_{1-y}O_2$ cathode materials [144, 161]. Other Mn oxidation states (Mn³⁺, Mn²⁺) detected on the surface of cycled NNMO samples are attributed to O vacancies [144], or to detrimental electrolyte decomposition occurring at the cathode/electrolyte interface [161]. As a matter of fact, alternative ionic liquid-based electrolytes are shown to effectively improve the cycle stability [161].



Figure 3.3: PBE+U(-D3BJ) electronic structure analysis of NNMO as function of Na content: net magnetic moments on **a**) Mn and **b**) Ni species, with the corresponding electronic configuration on the side; **c**) atom- and angular momentum- PDOS. Color code: Na s states in yellow, Mn d states in purple, Ni d states in green, O p states in red; **d**) Bader charge analysis reported as the average charge for each element; **e**) net magnetic moment on O atoms with corresponding electronic configuration on the side.

In any case, such variations are not related to the sodiation/desodiation

process. We must note that, in this material, real charges are far from the ionic limit, as a result of the high covalent character of TM-O bonds, due to the strong hybridization of TM d states with O p ones. This feature is evinced by the PDOS reported in Figure 3.3c. That being said, oxidation state variation trends upon desodiation are confirmed by the constant/increasing Bader charges for Mn/Ni species, respectively (Figure 3.3d). Figure 3.3e shows the trend of magnetization at O sites, which increases to ~0.3 μ_B at x = 0.25 and up to ~0.5 μ_B at x = 0.125, indicating a partial oxidation of O^{2-} species. The formation of electron holes on Oxygen atoms can be also identified from the PDOS, where O p states in the valence band cross the Fermi level, leading to a p-type character at x = 0.25and 0.125. Our findings are in close agreement with recent DFT and XAS results by Zhao *et al.* for the closely related $Na_{10-x}LiNi_3Mn_8O_{24}$ layered oxide, which indicate electron extraction taking place from Ni 3d states upon charge, and O 2p states starting to participate at high desodiation degrees [143]. In order to explore the O-redox activity in NNMO, we have first addressed the thermodynamics of Oxygen vacancy (V_O) formation. The removal of one Oxygen atom in our $4 \times 4 \times 1$ supercell corresponds to 1.56% of V_O concentration, which is in agreement with experimental records from a Li-based analogue [184]. As shown in Figure 3.4a, four types of vacancies have been considered, differing for both the coordination to the Mn-deficient site (first or second coordination shell, V_O (1) and V_O (2), respectively) and the chemical environment (Mn-O-Mn or Mn-O-Ni, $V_O(a)$ and $V_O(b)$, respectively). The V_O formation energy, E_{V_O} , has been computed according to Equation 3.2:

$$E_{V_O} = E_{def} - E_{prist} + \frac{1}{2}E_{O_2}$$
(3.2)

where E_{def} and E_{prist} are the total energies of O-defective and pristine NNMO, respectively, and E_{O_2} is the total energy of the Oxygen molecule as computed in its triplet ground state. Calculated values for each nonequivalent V_O at each Na content are listed in Table 3.2.

Table 3.2: Oxygen vacancy formation energies computed at the PBE+U(-D3BJ) level of theory according to Equation 3.2. Labelling is defined in Figure 3.4. V_O formation energies for the stoichiometric phase are also reported for comparison. All the values are expressed in eV.

x Na	Mn-deficient				stoichiometric	
	$\mathbf{V_O}(\mathbf{1a})$	$\mathbf{V_O(1b)}$	$\mathbf{V_O}(\mathbf{2a})$	$\mathbf{V_O}(\mathbf{2b})$	$\mathbf{V_O}(\mathbf{a})$	$\mathbf{V_O}(\mathbf{b})$
0.75	1.866	2.623	3.204	3.443	2.901	3.139
0.50	1.944	1.447	2.865	2.858	2.687	2.888
0.25	1.515	1.079	2.454	2.587	2.856	2.343
0.125	1.077	0.114	2.537	2.390	2.954	2.355

The results show that: (i) Oxygen vacancies are more likely to occur next to the Mn-deficient site rather than in the second coordination shell, as it is easier to remove a two-coordinated Oxygen atom than a three-coordinated one $(E_{V_O}(1^*) < E_{V_O}(2^*))$. Indeed, $V_O(1)$ -like vacancies are also more stable than three-coordinated V_O ones in the stoichiometric phase; (ii) there is

a general trend of decreasing formation energy with decreasing Na content due to charge compensation effects, leading to more favorable accommodation of reducing defects (V_O) in oxidized states (desodiated structures); (iii) $Mn-V_O$ -Ni configurations are more convenient than $Mn-V_O$ -Mn ones, as a result of the higher lability of the involved M-O bonds $(E_{V_O}(*b))$ $< E_{V_O}(*a)$). Even at low Na contents, breaking the Ni-O bond is still more favorable than breaking a Mn-O one, since the excess charge mostly delocalizes on the whole O sublattice (see corresponding panels in Figure (3.4b), leading to a significant defect stabilization [185, 186]; (iv) lower energies are found in the p-type Mn-deficient phase rather than in the stoichiometric one, which is consistent with the same charge compensation effect as stated in point (i). However, such effect can be less relevant when a large structural reorganization occurs, as in the case of $V_O(2a)$ configurations in Mn-deficient phase that are slightly less stable than $V_O(a)$ ones in the stoichiometric material. Overall, our computed E_{V_O} values are in the same energy range than for $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ [187]. The computed cumulative charge variation, Δq , on each element sublattice upon V_O formation is shown in Figure 3.4b. We have considered a threshold of $0.2e^{-}$ to establish a significant charge variation within a given sublattice. With this criterion, we can state that electrons left in the cell by the leaving Oxygen atom are mostly entering the Mn and O sublattices, regardless of the sodiation stage (purple and red diamonds in Figure 3.4b), while Na and Ni sublattices are not involved in the reduction. This is particularly true when the leaving Oxygen is not linked to Ni, that is $V_O(1a)$ and $V_O(2a)$.



Figure 3.4: a) Different kind of Oxygen vacancies considered in the present work. Color code as in Figure 3.1. Original positions of the leaving Oxygen are shown in pink. b) Cumulative charge variation upon vacancy formation, $\Delta q = q_{def} - q_{prist}$, for each sublattice plotted as function of Na content. Color code as in Figure 3.3d. The black dashed lines at $\Delta q = 0.2e^-$ is a guideline for the eyes to easily identify significant charge variations.

For V_O (1b)-kind of vacancy, only the O sublattice is significantly reduced at low Na contents. While the Oxygen contribution to Δq is extended
to the whole sublattice, reduction on Manganese atoms shows a very local character (see atom-resolved contribution to charge variations in Figure 3.5).



Figure 3.5: Atom-resolved contribution to charge variation upon O-vacancy formation from Mn and Ni atoms coordinating the vacancy in NNMO. Color code as in Figure 3.2.

As a matter of fact, no differences in the overall electronic structure can be detected among the different type of V_O (see PDOS in Figure 3.6).



Figure 3.6: Atom- and angular momentum- PDOS computed at the PBE+U(-D3BJ) level of theory for the O-defective NNMO materials. Color code as in Figure 3.3.

Inspired by the partial oxidation of some Oxygen atoms (Figure 3.3e) and the facility to create an Oxygen vacancy upon desodiation (Table 3.2), we have investigated the release of O₂ starting from the formation of diOxygen-metal compounds at low Na content. Figure 3.7 shows the stable O₂-intermediate structures identified at x = 0.25 and 0.125 after relaxation, and the corresponding energy variation, ΔE , given by Equation 3.3:

$$\Delta E = E_{dioxygen} - E_{NNMO} \tag{3.3}$$

where $E_{dioxygen}$ is the total energy of the O₂-intermediate within NNMO lattice and E_{NNMO} is the total energy of NNMO in its minimum-energy structure. Defined this way, negative ΔE values correspond to favorable formation of dioxygen-metal compounds from two regular Oxygen positions in the NNMO lattice. The A-D structures have been assigned to specific moieties according to M-O and O-O bond lengths and the geometry coordination, as illustrated in Table 3.3. At x = 0.25, all the O₂-intermediate structures consist of a superoxide species ($d_{O-O} \sim 1.26$ -1.29 Å, larger than d_{O-O} in O₂ but shorter than d_{O-O} in O₂²⁻) [188, 189], which coordinate the TM in different binding modes: in A and D configurations there is a similar bridging coordination of O_2^{2-} on two adjacent Ni and Mn atoms $(\mu^2 - \eta^1 - O_2)$; B configuration involves one binuclear bridging coordination of O_2^- to contiguous Mn atoms $(\mu - O_2)$; C configuration shows an end-on coordination of O_2^{2-} on a single Mn atom $(\eta^1 - O_2)$. The highest formation energy is found for the $\mu^2 - \eta^1 - O_2$ complex in D case ($\Delta E = 0.244 \text{ eV}$), which is associated to an Oxygen removal from the Mn-O-Mn site, while removing an Oxygen atom away from a Mn-O-Ni site always results to be easier (A, B and C cases). Amongst the four cases, the formation of $\mu^2 - \eta^1 - O_2$ complex in A is the most energetically favorable ($\Delta E = -0.097 \text{ eV}$), suggesting that the O-redox activity is already playing an important role at this state of charge. Since the x = 0.25 Na content can be assimilated to 4.1 V, this outcome explains the origin of the additional plateau exhibited during first charge cycle reported by Ma et al. [144]. At x = 0.125, two superoxide-based complexes have been identified: both configurations A and B are assigned to end-on coordination $(\eta^1 - O_2)$ on a Mn atom, with structure A showing the lowest (and negative) formation energy ($\Delta E = -0.431$ eV) due to the breaking of a Ni-O bond instead of a Mn-O one compared to structure B.



Figure 3.7: Dioxygen formation in NNMO: (top panel) top-view of A-D structures identified at a) x = 0.25 and b) x = 0.125. The yellow circles indicate the initial positions before dioxygen binding; (bottom panel) dioxygen formation energetics at a) x = 0.25 and b) x = 0.125. Side-views and moiety labels are also displayed according to the assignments reported in Table 3.3. Color code as in Figure 3.2, O atoms involved in the dioxygen-metal complexes are depicted in orange. Only atoms around the dioxygen complex are shown for clarity.

The C configuration, still bound but with large M-O distances, presents

a near-zero formation energy and a much shorter O-O distance (1.24 Å). Beyond the formation of these dioxygen-metal complexes, such low Na content enables also the complete release of molecular Oxygen: the D species features a O-O distance of (1.23 Å) and shows no direct coordination to any nearby TM atoms, with an unfavorable formation energy $\Delta E = \sim 0.8$ eV that is however easily accessible under NIB operating condition.

Table 3.3: O-O and M-O distances, d_{O-O} and d_{M-O} (Å), of dioxygenmetal complexes represented in Figure 3.7 at x = 0.25 (top) and x = 0.125(bottom) and corresponding assignment according to their coordination.

structure	$d_{\mathbf{O}-\mathbf{O}}$	$\mathbf{d}_{\mathbf{M}-\mathbf{O}}$	moiety	coordination
А	1.266	2.153(Mn)- $2.272(Ni)$	$\mu^2-\eta^1{-}O_2$	bridging
В	1.293	2.074(Mn)- $2.383(Mn)$	$\mu - O_2$	binuclear bridging
\mathbf{C}	1.289	2.022	$\eta^1 - O_2$	end-on
D	1.263	2.281(Mn)- $2.062(Ni)$	$\mu^2 - \eta^1 - O_2$	bridging
А	1.279	2.123	$\eta^1 - O_2$	end-on
В	1.288	2.155	$\eta^1 - O_2$	end-on
\mathbf{C}	1.243	2.575(Mn)- $2.575(Ni)$	$\mu^2-\eta^1{-}O_2$	bridging
D	1.231	-	O_2	molecular O_2

Alike O-O peroxo-like dimers have been visualized with TEM and neutron diffraction techniques in $\text{Li}_2\text{Ir}_{1-x}\text{Sn}_x\text{O}_3$ and have been ascribed to be responsible for the capacity gain in the Li-rich layered electrode [190]. These findings prove that O-redox activity in NNMO is triggered at very low sodiation stage, *i.e.*, high-voltage range, and that it likely occurs via formation of superoxide intermediates leading to the release of molecular O_2 . We have also provided some benchmark with hybrid functionals (see Section 5.1.1 for additional details). Formation energies of dioxygen complexes for x Na = 0.25 at the HSE06 level of theory are plotted in Figure 3.8 together with PBE+U ones.



Figure 3.8: PBE+U (blue) vs. HSE06 (red) benchmark of dioxygen formation in NNMO at x Na = 0.25

HSE06 results confirm the energy trend found with PBE+U. The convenient formation of dioxygen is even strengthened by the hybrid density functional. However, we must note that a single-point calculation with HSE06 with our numerical parameters and the VASP version we employed took \sim 52h on 480 CPUs (with IB connection), while the same calculations at the DFT+U took only few hours with the same computer power. For

this reason and considering the other DFT+U published results on similar systems [143, 158, 159, 172, 191], we believe that the accuracy/cost ratio of DFT+U makes it the most suitable approach to investigate systems and processes in our work. This compromise is rather important when one deals with large supercells (needed to model reasonable defect concentrations), dense k-points grid and very high plane-wave kinetic energy cutoff values. From a general perspective, the activation and control of reversible O^{2-}/O_2^{2-} reactions require the fine-tuning of all the constituent elements in the electrode. Substituting TM for d^0 or alkali metals, using cationdisordered structures as well as increasing the TM-O bond covalency are among the promising strategies to suppress an irreversible O_2 loss [140, 157, 160, 172]. We have shown that Mn-deficiency is required to enable anionic redox reaction, but at high voltage the labile Ni-O bond tends to release O₂ from the Mn-vacancy site via formation of low-energy superoxide intermediates. Indeed, implementing a stronger covalent nature for the TM-O bond via substitution of Ni with Fe has been recently proven to be effective [172]. Fe-doped P2-type $Na_x TMO_2$ cathodes exhibit enhanced specific capacities owing to reversible O^{2-}/O^{-} redox and no further evolution to molecular O_2 . Inspired by these evidences, we have also addressed the dioxygen formation in Fe-doped NNMO in order to provide direct comparison with results obtained for the NNMO material and endorse the design strategies outlined so far. We have considered the substitution of one Ni with one Fe atom in the Mn-deficient site, *i.e.*, where dioxygen formation takes place, corresponding to 3% at. of metal doping, for each



structure along the A-D series at both x = 0.25 and 0.125 Na contents.

Chapter 3

Figure 3.9: Dioxygen formation in Fe-NNMO: (top panel) top-view of A-D structures identified at a) x = 0.25 and b) x = 0.125. The yellow circles indicate the initial positions before dioxygen binding; (bottom panel) dioxygen formation energetics at a) x = 0.25 and b) x = 0.125. Side-views and moiety labels are also displayed according to the assignments reported in Table 3.4. Color code as in Figure 3.7, Fe atoms are depicted in light blue. Only atoms around the dioxygen complex are shown for clarity.

As illustrated in Figure 3.9a, at x Na = 0.25 a bridged-superoxide moiety binding to Mn and Fe atoms can form spontaneously, thus confirming that anionic activity is enabled for Fe-NNMO at this state of charge (~4.0 V) [172]. Figure 3.9b shows that two stable structures are identified at xNa = 0.125, namely A and C, the former being end-on coordinated to Fe and the latter bridged to Fe and Mn atoms. Structural details and moiety assignments are listed in Table 3.4. Different from NNMO, all the explored cases present coordinated dioxygen moieties (M-O distances ranging from 2.01 to 2.61 Å) with O-O distances ascribed to superoxide-like O_2 , never reaching the status of free O_2 . Thus, Fe-doped NNMO is predicted to present both Oxygen activity and reduced O_2 release.

Table 3.4: O-O and M-O distances, d_{O-O} and d_{M-O} (Å), of dioxygenmetal complexes in Fe-NNMO represented in Figure 3.9 at x = 0.25 (top) and x = 0.125 (bottom) and corresponding assignment according to their coordination.

structure	$d_{\mathbf{O}-\mathbf{O}}$	$\mathbf{d}_{\mathbf{M}-\mathbf{O}}$	moiety	coordination
А	1.277	2.083(Mn)-2.309(Fe)	$\mu^2 - \eta^1 - O_2$	bridging
В	1.299	2.010(Mn)- $2.279(Fe)$	$\mu^2 - \eta^1 - O_2$	bridging
С	1.298	2.011(Mn)- $2.297(Fe)$	$\mu^2 - \eta^1 - \mathcal{O}_2$	bridging
D	1.267	2.169(Mn)-2.179(Fe)	$\mu^2 - \eta^1 - O_2$	bridging
А	1.255	2.472 (Fe)	$\eta^1 - O_2$	end-on
В	1.345	2.056 (Mn)	$\eta^1 - O_2$	end-on
С	1.265	2.445(Mn)-2.472(Fe)	$\mu^2 - \eta^1 - O_2$	bridging
D	1.253	2.492(Mn)-2.606(Fe)	$\mu^2 - \eta^1 - O_2$	bridging

As in NNMO, the energy differences among the A-D structures seems to rely on the O departure position (highlighted in top panels of Figures 4 and 5). Oxygen vacancy formation seems to be correlated to the O_2 evolution, as it provides direct information on the tendency to loose an Oxygen atom that form a dioxygen compound. We have computed the Oxygen

vacancy formation energies in Fe-doped NNMO at x Na = 0.125. For twocoordinated $V_O(1)$ -like vacancies in three possible configurations, we have obtained the following formation energies: $2.253 \text{ eV} (\text{Mn-}V_{O}\text{-Mn}), 1.755$ eV (Mn- V_O -Fe) and 1.533 eV (Mn- V_O -Ni). These values are ~ 1 eV higher than corresponding formation energies in NNMO (1.077 eV for $Mn-V_O-Mn$ and 0.114 eV for $Mn-V_O-Ni$, suggesting that Fe doping leads to an overall stabilization of the oxide lattice. On the other hand, this trend shows that breaking Fe-O bond is easier than Mn-O but more difficult than Ni-O one. The Fe-O bond is less labile than Ni-O and it effectively allows to inhibit O_2 release in the high voltage range, but dioxygen can still form. In this way, not only extra specific capacity can be achieved, but it can also be recovered upon subsequent charge/discharge cycles since O_2 release is suppressed or at least reduced. While a general picture of O-redox activity is rapidly taking shape [158, 159], our new insights on NNMO highlight simple descriptors (Oxygen vacancy formation and TM-O₂ coordination energy) that could be able to predict the Oxygen evolution in a given structure and the critical state of charge for the irreversible material degradation. This thorough investigation on the P2-type Mndeficient $Na_x Ni_{0.25} Mn_{0.68} O_2$ layered oxide provides new theoretical insights into the charge compensation mechanism driven by partially oxidized Oxygen atoms and suggested by experiments. Some important aspects can be highlighted:

– accurate electronic structure analysis on NNMO revealed that desodiation is coupled to $Ni^{2+} \rightarrow Ni^{3+}$ oxidation and, when the state of charge goes up to 4.5 V, further oxidation to Ni⁴⁺ with a noninnocent contribution of O²⁻ takes place, while Mn⁴⁺ does not participate, in agreement with the available experimental observations. Increased magnetization on O atoms and p-type character of the material at x = 0.125 composition confirm that stable Oxygen electron holes can be formed in NNMO at 4.5 V;

- Oxygen vacancies are more likely to form nearby the Mn-deficient site at low Na content (x = 0.125, *i.e.*, 4.5 V state of charge), preferably along Mn-O-Ni bonds than along Mn-O-Mn ones;
- the low-energy superoxide-based structures at x = 0.25 act as possible intermediates toward the formation of molecular O₂. An Oxygen molecule is expected to be released from a Mn-deficient site at x = 0.125 with preferential breaking of Ni-O bond;
- Fe substitution leading to increased TM-O covalency in NNMO is shown to be effective toward the stabilization of the oxide lattice and possible suppression of O₂ release.

These findings set clear directions for further research to prevent O_2 release and feature simple descriptors (Oxygen vacancy formation and TM- O_2 coordination energy) that could be helpful in predicting the evolution of Oxygen redox activity. Future research efforts need to focus on different TM ions on the O_2 formation mechanisms and to chase the complete characterization of $O^{2-}/O_2^{2-}/O_2$ evolution mechanism from the bulk to the exposed surfaces. We believe that atomistic details on these processes can provide the scientific community with new rational design strategies for advanced and more efficient P2-type Na_xTMO_2 that are able to recover the extra specific capacity in subsequent charge/discharge cycles, paving the route towards the application of these promising cathode materials in high-performing Na-ion batteries. The outcomes of this study are the object of a research article published on *ACS Energy Letters* journal in 2021 [192].

4 Ionic transport through the electrolyte

In the materials development for the assessment of high-efficiency NIB devices, novel electrolytes that are safe, reliable and easily recyclable need to be optimized. Solid polymer matrices [193] and RT-ILs [194] can replace the currently used liquid electrolytes in several formulations [195, 196]. RT-ILs emerged as valid alternatives to common organic solvents because of their unique properties, including virtually no volatility, non-flammability, high thermal and electrochemical stability, that would enhance the sustainability of manufacture processes, the device operation and cycle life. Since the discovery of the first ionic liquid [197], the interest for this family of materials increased strongly in both academia and industry [198], covering a wide range of applications, from solvents for reactions, separations and materials processing [199, 200], to electrolytes for energy-storage devices [201], but also lubricants [202] or plasticizers [203]. On one hand, understanding the Na⁺ transport through RT-ILs is key to design novel

electrolyte materials for NIBs. RT-ILs are low-melting organic salts and highly structured fluids with complex interactions arising from the variety of chemical groups composing the ions. Modeling these complex interactions is challenging but can be very helpful to investigate how molecular interactions and local ordering affect relevant physico-chemical such as ionic transport. On the other hand, assessing their use as plasticizers to realize conductive polymeric membranes is also required to boost the development of high-performing solid state electrolytes. In the following sections, we are going to discuss our contribution in this context, concerning both theoretical advances for improved description of Na⁺ transport in RT-IL based systems that have been achieved during the 6-months research stage in the group of Prof. Pádua at the École Normale Supérieure de Lyon (Section 4.1), and electrochemical tests of RT-IL/PEO-based polymer electrolytes in combination with innovative electrode materials that have been carried out during the 9-months stage in the R&D laboratories of Lithops S.r.l. in Turin (Section 4.2).

4.1 The explicit polarization in RT-IL based electrolytes

Atomistic MD appears as a highly suitable methodology to investigate the structure-property relationship in RT-IL based electrolytes from a molecular-scale point of view. MD is based on a detailed description of the molecular structures and interactions (the atomistic force field) and

covers ranges of time (10 to $100 \,\mathrm{ns}$) and length (10 to $100 \,\mathrm{nm}$) scales that are suited to study microscopic ordering, dynamics and energetics of condensed phases [204, 205], treated as extended systems with periodic boundary conditions (see Section 5.2 for further details). At the present state-of-the-art in theoretical methods and computational power, quantum mechanical calculations with the required accuracy would be limited and not affordable in computational cost for the aforementioned time and length scales that typically characterize the ordering and dynamics of ionic liquids. MD simulations of RT-ILs have led to the awareness that both structure and dynamics are very sensitive to the representation of electrostatic interactions. Both equilibrium and transport properties in these systems strongly depend on details of non-covalent interactions, namely the balance between Coulomb and van der Waals forces [206–208]. Describing Coulomb interactions by means of fixed partial charges on the atomic sites (with integer ionic charges) is common practice in atomistic force fields and has been successful in predicting thermodynamic properties. However, the dynamics turns out to be too slow (viscosity too high) when compared to experiments [209]. One possible workaround has been to scale ionic charges (and thus each atomic partial charge) by a factor of about 0.8 [210–212]. Such a scheme allows faster dynamics due to the diminished Coulomb interactions, but the reduction in cohesive energy leads to issues with structural and volumetric properties, *i.e.*, the density will become too low and features of near-neighbor structure will become attenuated [213]. The possibility of including explicit polarization in classical

atomistic force fields for ionic liquids has changed this scenario recently, bringing significant improvements in the predictive power of MD simulations [214]. This approach is at the boundary between quantum (electronic structure) and classical levels, since it represents the response of electron clouds (via charge distributions) to their electrostatic environment. In ionic liquids, composed of large molecular ions, polarizability is expected to play an important role in adjusting the electron density and thus an explicit treatment of induction should greatly improve models [213].

Herein, an application of a polarizable model for a mixed salt/RT-IL system (NaFSI-Pyr₁₃FSI) is reported as case-study. We have investigated physico-chemical properties that can be relevant to assess the suitability of this system as electrolyte for NIBs. Our study show that addition of explicit polarization is required to attain a reliable description of Sodium transport properties. New insights from MD simulations are provided together with experimental results that are used to validate the theoretical predictions. Despite its lower thermal and electrochemical stability when compared to its TFSI counterpart, the $\mathrm{Pyr}_{\mathrm{13}}\mathrm{FSI}$ ionic liquid has been widely used in batteries, mainly LIBs, due to its remarkable SEIforming ability and lower viscosity accounting for enhanced ionic conductivity [215–217]; still, ongoing efforts are focused on the understanding of ion transport characteristics. Actually, gaining a proper understanding of the fundamental chemistry that occurs upon addition of the Sodium salt to the ionic liquid to predict its speciation and interactions with the bulk solvent is fundamental to develop advanced, high-performing NIB systems employing RT-IL based electrolytes. In this respect, the extensive study reported by Chen *et al.* [218] has shown an unexpected behavior of Na⁺ diffusion as a function of concentration in the same RT-IL system. According to the Walden rule (Equation 4.1), ionic conductivity, Λ , (which accounts for ion mobility) should be roughly inversely proportional to viscosity, η , for the same ions in different solvents:

$$\Lambda \eta = \text{const.} \tag{4.1}$$

The study of Chen *et al.* [218] reports non-monotonous diffusion coefficients of Na⁺ as a function of concentration in $Pyr_{13}FSI$, despite one would expect that with increasing Na salt concentration the viscosity increases and consequently ion diffusion slows down monotonously. Thus, only some marked association or solvation interactions imparting a strong deviation onto the dynamics of Sodium could justify such behavior. While previous data have been obtained with fixed, scaled-charge force fields [218], we have inquired if similar results could be also observed using a polarizable force field. To this end, we focus on Na⁺ diffusion in $Pyr_{13}FSI$ by comparing theoretical results obtained from either fixed scaled-charges and polarizable force fields, and providing direct comparison with experimental data, including density, viscosity and diffusion coefficients measured by DOSY-NMR technique. For additional information on the simulation details, we refer the interested reader to Section 5.2.3, while the aforementioned

experimental techniques are described in Section 5.3.1. Theoretical selfdiffusion coefficients have been derived from mean-squared displacements (MSD) using the Einstein relation:

$$D = \lim_{t \to \infty} \frac{1}{6} \frac{d}{dt} \left\langle (r(t) - r(0))^2 \right\rangle \tag{4.2}$$

We have extracted the MSD of Pyr_{13}^{+} and FSI⁻ from the 8 ns-trajectory of the pure RT-IL and linearly fitted the plot in its diffusive regime (from 2 to 8 ns, see Figure 4.1a) [219]. The results obtained from both fixed scaled-charges and polarizable trajectories are reported in Table 4.1.

Table 4.1: Density, ρ (g cm⁻³), and self-diffusion coefficients, $D_{Pyr_{13}}^{+}$ and $D_{FSI^{-}}$ (m² s⁻¹), calculated with both fixed scaled-charges (ScaleQ) and polarizable force fields (Drude) at 353 K. Experimental data from Ref. [220] at 353 K are reported for comparison.

method	ho	$\mathbf{D}_{\mathrm{Pyr}_{13}^{+}}^{+}$	$\mathbf{D}_{\mathrm{FSI}^-}$
exp^*	1.295	14.0×10^{-11}	17.0×10^{-11}
ScaleQ	1.254	2.71×10^{-11}	3.20×10^{-11}
Drude	1.275	7.08×10^{-11}	7.84×10^{-11}

From the values listed in Table 4.1, we can confirm that the polarizable model gives more reliable predictions of both density and diffusion compared to the fixed scaled-charges one, showing better agreement with experimental data reported in the literature [220]: the deviation from experimental density are -1.5% and -3.2% for Drude and ScaleQ models,

respectively; self-diffusion coefficients are lower than the experimental ones by a factor of 2 when using Drude model, while even lower (by factor of 5 to 6) with the fixed and scaled-charge force field. Moving to the binary salt/RT-IL system, we have computed the self-diffusion coefficients of all the ions present in the systems. We have also calculated the viscosity as described in the literature [221]. After performing a scan of reasonable \mathcal{A} values on one system, we have selected the 0.02×10^{-5} Å fs⁻² value to compute viscosities at each composition. The diffusion and viscosity results are shown in Figure 4.1b and Figure 4.2b, respectively. For each ionic species, we observe a monotonous decrease of self-diffusion coefficients as a function of salt concentration, consistently with the Walden rule, Equation 4.1.



Figure 4.1: a) MSD of Na^+ obtained from polarizable trajectories and plotted as function of time for each salt content. b) Plot of self-diffusion coefficients, D, as function of composition, x [NaFSI], at 353 K computed for each ionic species from MD simulations using the polarizable force field.

Direct comparison to experimental results is provided in order to validate

our theoretical results obtained from MD simulations using the polarizable force field. Despite extensive characterization of these systems already exists and several experimental data have been previously reported in the literature [220, 222, 223], we have set up density, viscosity and diffusion coefficients experiments in order to have a more systematic and precise experimental reference for our theoretical outcomes. Self-diffusion coefficients of Pyr_{13}^{++} and FSI^{-} ions have been obtained by DOSY-NMR technique at room temperature, while density and viscosity have been determined in a wide temperature range, so that in principle diffusion coefficients at any other temperature could be extrapolated for direct comparison to MD simulations. We will discuss this approach later in the text. For the prepared samples (see Table 5.1 in Section 5.3), we have measured density and viscosity and reported the results in Figure 4.2. Density data have been linearly fitted as a function of temperature and present an absolute average deviation from the fits lying between 0.007% and 0.01%. Viscosity data (reported in Figure 4.2b as the log of viscosity, where viscosity is given in mPas) have been fitted using the Vogel-Fulcher-Tammann-Hesse (VFTH) equation [224], with an absolute average deviation lying between 0.1% and 4%. Both density and viscosity naturally decrease with the temperature in each solution, while an increasing trend with the salt concentration is shown at all temperatures: higher values are observed going from the pure ionic liquid (black line) and the solution containing x = 0.1 Na salt (pink line), while a pronounced increase is detected from x = 0.1 to x = 0.3(green line) and even more from x = 0.3 to x = 0.5 (blue line). While our experiments stop at x = 0.5 molar fraction due to solubility issues [223], we have performed MD simulations at x = 0.9 as proof of concepts to show the monotonous trend of self-diffusion coefficients beyond the limit of salt solubility [218].



Figure 4.2: Plots of experimental **a**) density, ρ , and **b**) viscosity, η , of NaFSI-Pyr₁₃FSI solutions as function of temperature, T, measured for each composition. Dashed lines show the linear and VFTH fits to density and viscosity, respectively. Experimental densities from literature [220, 222] (triangles, panel a), as well as densities and viscosities from simulation (squares, panel a and b, respectively) obtained in this work using the polarizable force field are also reported for comparison.

We have recorded the DOSY-NMR spectra for each solution (Figure 4.3). By looking at the ¹H-NMR spectrum (top panel of Figure 4.3), an overall shift to lower δ is detected with increasing concentration [225] (as highlighted in the inset along the spectrum), whereas in the ¹⁹F-NMR spectrum (bottom panel of Figure 4.3) we first observe a shift from 52.55 ppm in the pure ionic liquid (black line) up to 52.70 ppm for x = 0.3 (green line), but then it goes down to 52.65 ppm when going to the x = 0.5 composition



Figure 4.3: (left) ¹H and (right) ¹⁹F NMR spectra of the sample solutions recorded at 298 K. Inset: zoomed-up region from ¹H spectrum.

(blue line). A possible interpretation of the observed variations in chemical shifts with increasing salt concentration can be provided by looking at the shielding factor, which is a measure of the electron density around the nuclei and thus directly affects the chemical shift. There are several terms that contribute to the shielding factor, such as the induced diamagnetic and paramagnetic electronic movement, anisotropy and electric field, which accounts for the electronic circulation in the entire molecule [226]. We can say that the larger transfer of electron density from anions to cations occurring at higher Na salt concentrations can account for the overall decrease of ¹H δ values and increase of ¹⁹F ones till the x = 0.3 composition. However, in the most concentrated system the solvation structure among anions is even tighter, which enhances the surrounding electron density and thus leads to the decreased $^{19}\mathrm{F}~\delta$ value.

Table 4.2: Diffusion coefficients, $D_{Pyr_{IS}^+}$ and D_{FSI^-} (m² s⁻¹), determined from DOSY-NMR experiments at 298 K.

sample	$\mathbf{D}_{\mathrm{Pyr}_{13}^{+}}^{+}$	$\mathbf{D}_{\mathrm{FSI}^-}$
pure RT-IL	3.27×10^{-11}	3.44×10^{-11}
0.1 NaFSI	2.35×10^{-11}	2.57×10^{-11}
0.3 NaFSI	1.07×10^{-11}	1.10×10^{-11}
0.5 NaFSI	4.06×10^{-12}	2.69×10^{-12}

The solvation structure of the salt/RT-IL system is discussed further in the text. The DOSY-NMR experiments allow the determination of selfdiffusion coefficients of both cation and anion at each concentration and at 298 K. From the data reported in Table 4.2, we observe a slight decrease until x = 0.3 and a more important lowering by an order of magnitude at x = 0.5, which correlates well with the large increment in viscosity (Figure 4.2). The so-obtained self-diffusion coefficients at 298 K together with the viscosities measured at several temperatures have enabled the direct comparison to simulation-derived values. Extrapolation of the experimental self-diffusion coefficients at 353 K through viscosity taken at 298 K and 353 K can be done according to Equation 4.3, which is easily derived from the well-known Stokes-Einstein law, *i.e.*, $D = k_B T/(6\pi\eta r)$.

$$\frac{D(T_1)\eta(T_1)}{T_1} = \frac{D(T_2)\eta(T_2)}{T_2}$$
(4.3)

We have plotted the extrapolated self-diffusion coefficients, D(353 K), together with the theoretical ones obtained from both polarizable and nonpolarizable models as function of Na salt content, as shown in Figure 4.4.



Figure 4.4: Plot of self-diffusion coefficients, D, for cation (blue squares) and anion (red diamonds), as obtained from DOSY-NMR experiments via extrapolation to 353 K (solid line) and MD simulations with polarizable Drude model (dashed line) and non-polarizable ScaleQ model (dotted line) as function of composition, x [NaFSI].

Not only self-diffusion coefficients obtained from the polarizable model are closer to the experimental values, but also the steep decreasing trend with Na salt content is better reproduced when polarization is taken into account. We can assess the significant beneficial effect of including explicit polarization in describing Na transport properties and its crucial role in reconciling the increase in viscosity with the decrease of diffusion of all the ions while the salt content is augmented in the RT-IL based solution. In order to extract structural information that can be useful to examine the solvation shells around Na⁺, we have computed the radial distribution function (RDF) of Oxygen atoms from FSI⁻ around Na⁺ and the corresponding coordination numbers (CN) for each explored composition, with both the fixed-charges and polarizable model (Figure 4.5, panels a and b, respectively).



Figure 4.5: RDF of $Na-O_{FSI}$ (solid lines) and corresponding coordination number (dashed lines) obtained with the **a**) ScaleQ and **b**) Drude models. Inset: structural detail of Na-O coordination at 2.35 Å (first peak of the RDF).

The RDF from the Drude model (Figure 4.5b) shows the first peak at 2.35 Å, representing either monodentate and bidentate geometries (Figure 4.8). Integration of the RDF to the first valley, *i.e.*, to 3.25 Å, leads to CN values increasing from 4.9 to 5.5 when mole fraction of Na salt varies from 0.1 to 0.9. By comparing Figure 4.5a and Figure 4.5b, we can clearly see that when polarization is included the RDF results in narrower and left-shifted peaks, and it is possible to detect an increase in the coordination number upon concentration. We have also explored other

possible Na-anion interactions by looking at RDFs with different coordinating atoms from FSI⁻, *i.e.*, Nitrogen and Fluorine. The RDF of Na-N pairs, Figure 4.6a, shows the first peak at 2.45 Å corresponding to a Nmonodentate coordination that is stabilized by the neighbor Oxygen with a very low CN (~0.3). On the other hand, the peak at 4.65 Å gives a CN (obtained by integrating up to 5.55 Å) increasing from 4.5 to 5.4 when the salt concentration goes from 0.1 to 0.9. In the RDF of Na-F pairs (Figure 4.6b), the peak at 4.40 Å gives CN from 5.6 to 8.1 (integration up to 5.25 Å). The first Na solvation shell seems to be dominated by Oxygen, while Nitrogen and Fluorine are displaced further. The coordination number always increases with Na content, as a result of the larger number of Na⁺-FSI⁻ ion pairs.



Figure 4.6: RDF (solid lines) and corresponding coordination number (dashed lines) of (a) $Na-N_{FSI}$ and (b) $Na-F_{FSI}$ distances.

In order to have a 3D-view of the solvation shells and to see to what extent they change with increasing salt content, we have computed the spatial distribution function (SDF) (illustrated in Figure 4.7), which are isodensity maps of selected atoms around a central molecule or ion, averaged over a MD trajectory. FSI⁻ has been chosen as the central ion and the SDF has been calculated considering three target atom types, namely Na, $N(Pyr_{13})$ and N(FSI). In Figure 4.7 we see that FSI⁻ is always surrounded by Na⁺ at close distances, even at low Na-salt concentration, while Pyr_{13}^{+} is found at slightly longer distances, due to the larger size of the pyrrolidinium cation. As a result of cation-separated solvation, FSI⁻ anions stay closer to the central anion when the smaller Na⁺ becomes the most abundant cation in the mixture, meaning that FSI-FSI correlations become stronger and anion ordering is more marked at higher salt concentrations.



Figure 4.7: SDF of FSI⁻ (blue), Pyr_{13}^{+} (cyan) and Na^{+} (purple) around central FSI⁻ at different compositions. Atomic density for both FSI⁻ and Pyr_{13}^{+} has been calculated with respect to Nitrogen. The isosurface is plotted at 1.7, 4.5 and 7.3 times the average density of FSI⁻, Pyr_{13}^{+} and Na^{+} , respectively.

This can also be seen in the RDF of $N_{FSI}-N_{FSI}$ reported in Figure 4.8 and it is in agreement with the analysis of the ¹H and ¹⁹F NMR spectra based on the electron density around the ions. Looking at the Na–FSI SDF (purple blobs), a less spread-out distribution is detected at x = 0.9 (on the very right side of Figure 4.7) when compared to less concentrated systems, suggesting a stronger Na⁺-anions interaction, which most likely accounts for lower Na⁺ mobility.



Figure 4.8: a) RDF of $N_{FSI}-N_{FSI}$ distances computed from polarizable MD trajectories for each salt composition. b) Penta- and hexa-coordinated geometry around Na with, respectively, one and two bidentate FSI⁻ anions. Color code: Na in pink, O in red, S in yellow, N in blue and F in green. Main distances are displayed.

All the insights provided throughout this study can be summed up as follows:

 including polarization explicitly in the force field improves the reliability of the predicted properties, especially when it concerns large molecular ions interacting via non-covalent forces. Our polarizable model for the NaFSI-Pyr₁₃FSI system is compared to commonly adopted non-polarizable model: more accurate predictions of dynamic properties and structural quantities are provided if polarization is taken into account;

- direct comparison of theoretical predictions with experimental results represents an unambiguous way to outline the relevance of polarization in MD simulations. Both physico-chemical characterization (in terms of density and viscosity) and diffusion coefficients from pulse field gradient NMR experiments are reported;
- structural analysis of solvation layers has revealed that Na⁺ mobility could be inhibited at higher concentration due to formation of tight Na⁺-FSI⁻ ion pairs.

The polarizable force field used for the present molecular simulations has been constructed aiming for transferability and generality, in order to represent different properties of a large variety of ionic liquids and related systems, and also to be compatible with models for molecular compounds and materials. It has been used here without specifically parameterizing the interactions of Sodium with the ionic liquid. We are aware that more specific models can lead to closer agreement with experiment [227, 228]. However, we have shown that our polarizable model largely improves the description of transport-related properties compared to stateof-the-art non-polarizable force fields. Our study may contribute to future works aiming to investigate similar RT-IL based electrolytes for important applications in novel energy-storage and sensor technologies. The use of polarizable force fields can be extended to even more complex materials where the atomistic description is key to unveil the mechanism of Sodium transport. The results discussed so far have been published in the *Physical Chemistry Chemical Physics* journal in 2020 [229].

4.2 Electrochemical behavior of RT-IL/PEO based electrolytes: practical lab-scale cell testing

In the material research focused on electrolytes for NIBs, polymer-based systems have attracted special attention owing to good mechanical properties, high thermal stability, wide electrochemical stability windows and compatibility with the electrodes, thus meeting most of the fundamental requirements for next-generation reliable large-scale devices. The relatively inert poly(ethylene oxide) - PEO is the most widely investigated polymer for battery applications. The formation of stable complexes with Li/Na salts makes PEO a promising host material in electrolyte formulations [230–233]. The ionic conductivity seems to rely on amorphous domains, while highly symmetrical ethylene oxide (EO) units coordinating Li/Na salts tend to crystallize and slow down the ionic diffusion [234, 235]. Using room-temperature ionic liquids (RT-ILs) as additives in PEObased formulations has appeared as a possible strategy to promote ion mobility [204, 236–239], since they feature large (soft) anions that would easily release the small (hard) $\mathrm{Li^+/Na^+}$ from the strong EO coordination. RT-ILs can act as plasticizers in the polymer matrix, thus mitigating the increase of glass transition temperature induced by salt addition [232]. On the other hand, the chance to modify the microscopic network of the polymer matrix via light-driven free-radical polymerization process (UV-curing) has enabled the easy and eco-friendly synthesis of quasi-solid and eco-friendly electrolyte films with self-standing ability. Investigating the chemical composition and preparation techniques that allow good Na⁺ transport and efficient sodiation/desodiation processes is essential to boost the application of RT-IL/PEO-based electrolytes in NIB. In this context, we have set up the electrochemical characterization of novel electrolytes with different composition, the most promising candidates being tested in lab-scale NIB prototypes with state-of-the-art electrode materials. The work carried out so far can pave the route for future studies aiming at the implementation of these safe and reliable electrolytes in real-scale full cells. Two different RT-ILs, N,N-methylbuthyl pyrrolidinium bis(fluorosulfonyl) imide $(Pyr_{14}FSI)$ and 1-ethyl-3-methyl imidazolium bis(fluorosulfonyl)imide (EmiFSI), have been employed in combination with sodium bis(fluorosulfonyl)imide (NaFSI) as salt to obtain liquid electrolytes with 6:1 RT-IL:salt molar ratio. We have first performed the galvanostatic cycling (GC) of Na-metal cells with hard carbon (HC) anodes and $Na_3V_2(PO_4)_2F_3$ (NVPF) cathode with these two electrolytes in order to select the best RT-IL candidate to be combined into polymer electrolytes (see Section 5.3.2 for further details on the employed materials, cell assembly and GC experiments). We have employed two HC-based compounds obtained by pyrolysis of two unique bioderived nanomaterials, *i.e.*, exhaust coffee and cellulose nanocrystals (namely HC_Coffee and HC_CNC, respectively) deriving from the most abundant natural polymer, cellulose, and normally discarded as organic waste. The so-obtained products have previously undergone an activation step: addition of KOH enables the intercalation of hydroxyl groups into the carbonaceous matrix, thus creating suitable domains that can act as Na⁺ hosts. In general, the theoretical capacity of an intercalation-active material is defined as:

$$Q_{th} = \frac{nF}{3600M_w} \tag{4.4}$$

where *n* is the number of charges inserted upon discharge, *F* is the Faraday constant and M_w is the molecular weight of the system. Due to structural complexity and variability of hard carbon matrix, theoretical capacity can only be estimated [240]. We have considered a value of 300 mA h g⁻¹ for the HC anodes and calculated the relative C-rate depending on the effective mass of the active electrode material. All the tests with liquid electrolytes have been performed at RT and C/10 rate, corresponding to 44.1 µA cm⁻² and 48.3 µA cm⁻² for HC_Coffee and HC_CNC, respectively. The corresponding GCs are reported in Figure 4.9. For each sample, the voltage vs. specific capacity profiles shown in Figure 4.9a appear as smooth curves, typical of amorphous materials where sodiation/desodiation does not occur at precise voltage values. Comparison of Emi- and $Pyr_{14}FSI:NaFSI$ in HC_Coffee cells reveals that the specific capacity output is similar, but the pyrrolidinium-based electrolyte leads to higher capacity retention compared to the imidazolium one (93.9% > 92.6% for, respectively, Pyr- and EmiFSI:NaFSI), which also outpaces a conventional electrolyte containing PC:NaClO4 (87.1%), that we have measured in similar conditions in order to have a direct reference.



Figure 4.9: Galvanostatic cycling of HC-based Na metal cells with liquid electrolytes: a) Voltage vs. specific capacity profiles for selected cycles. The first cycle is shown in the inset; b) plots of specific charge capacity (red) and Coulombic efficiency (green) vs. cycle number.

HC_CNC can achieve much higher capacity values (up to $150 \,\mathrm{mA}\,\mathrm{h}\,\mathrm{g}^{-1}$), even though capacity retention needs to be improved (90.2%). The same

liquid electrolytes have been tested with NVPF cathode. In principle, this material can exchange three equivalents of Na⁺ at different voltage values. It is noteworthy that in this case, the active material features a crystalline structure where sodiation/desodiation takes place at specific voltage values, thus leading to voltage vs. specific capacity plots with neat and welldefined plateaux. Anyway, it has been recently reported that the third Sodium ion within the NVPF structure is accessible at very high potential $(\sim 4.8 \text{ V vs. Na}^+/\text{Na})$ and it is coupled to the formation of a new tetragonal phase [241]. Yan *et al.* suggest that the disordered Na occupancies in this polymorph would lead to different sodiation/desodiation mechanism: the third Sodium ion is effectively re-intercalated if the new NVPF phase is discharged to $\sim 1.6 \text{ V}$ vs. Na⁺/Na, instead [241]. For our tests with liquid electrolytes that can be cycled within 2.8-4.2 V, we have first calculated the theoretical capacity corresponding to the extraction of 2 Na⁺ (n = 2in Equation 4.4), which results in $129 \,\mathrm{mA}\,\mathrm{hg}^{-1}$, and performed the GC runs with both liquid electrolytes at RT and C/10 rate, corresponding to $11.4 \,\mu A \,\mathrm{cm}^{-2}$. As shown in Figure 4.10a, the Emi-based electrolyte results in an extremely short cycling, with only two stable charge/discharge cycles followed by a very early capacity drop and related cell failure. Conversely, a promising profile is observed with the pyrrolidinium-based cell; the stability of the Pyr-based RT-IL has also allowed to explore higher voltage ranges during the GC run, as shown in the corresponding voltage vs. time profile in Figure 4.10a. Figure 4.10b shows the voltage vs. specific capacity profiles of selected cycles featuring different cut-off voltage values (highlighted by dashed lines in the plot). Pushing the cut-off voltage up to 4.4 V has effectively enabled the intercalation/extraction of 2 Na⁺, as clearly shown by the increasing capacity in Figures 4.10b (10th vs. 20th cycle) and 4.10c (after 15 cycles).



Figure 4.10: Galvanostatic cycling of NVPF-based Na metal cells with liquid electrolytes: **a**) Voltage vs. time profiles of EmiFSI:NaFSI and $Pyr_{14}FSI:NaFSI$ electrolytes; **b**) Voltage vs. specific capacity for selected cycles (first cycle is shown in the inset) of $Pyr_{14}FSI:NaFSI$ cell; **c**) Specific discharge capacity (blue) and Coulombic efficiency (green) vs. cycle number of $Pyr_{14}FSI:NaFSI$ cell.

In an attempt to achieve the third sodiation plateau, we have reset the

cut-off voltage limits at 1.4-5 V, but no phase transition has been observed and the capacity gain was extremely low due to the incomplete deintercalation of third Sodium ion (see Figure 4.10b, 30^{th} cvcle, pink line, and Figure 4.10c). From these observations, we have inferred that the use of RT-ILs with lower conductivity compared to conventional carbonates - employed in Ref. [241] - would increase the overpotential and thus require even higher voltage to enable the phase transition and the following third-sodium deintercalation. However, these results only represent preliminary investigations on NVPF/RT-IL systems and an in-depth understanding of their electrochemical behavior will be addressed in the next future. The scope of this Thesis work is to define the working conditions for polymer electrolytes applied in lab-scale NIB prototypes. Further tests with PEO-based materials have been performed by keeping the cut-off voltage at $4.5 \,\mathrm{V}$ in order to preserve the electrolyte and ensure a more stable long-term cyclability (see Figure 4.14 and further discussion below). Overall, the capacity retention is promising and even higher compared to conventional electrolyte, that we have measured to provide direct comparison (96.5% vs. 87.9% of PC:NaClO4). As for the above discussion, pyrrolidinium-based electrolyte has shown better capabilities than the imidazolium one, especially on the cathode side, thus being selected to prepare polymer electrolytes. We have added PEO and benzophenone (BP) to two solutions of $\mathrm{Pyr}_{14}\mathrm{FSI:NaFSI}$ with different concentrations, i.e.,4:1 and 6:1 RT-IL:salt molar ratio, leading to PEO Pyr4 and PEO Pyr6, respectively. BP is a hydrogen-abstracting photoinitiator, which serves to
induce the cross-linking between polymer chains upon UV-curing procedure [242]. Characterization of polymer electrolytes has been carried out in terms of electrochemical stability and ionic conductivity (see Section 5.3.2 for additional information on polymer electrolytes preparation and characterization techniques). The former can be determined from cyclic voltammetry (CV) profiles, that we have recorded at room temperature in both anodic and cathodic regimes, as reported in Figure 4.11.



Figure 4.11: Electrochemical stability windows of PEO_Pyr4 (blue) and PEO_Pyr6 (green): current density in the anodic (top panels) and cathodic (bottom panels) regimes plotted as function of voltage.

Carbon coated aluminum (CC-Al) has been used for the determination of the ASW, so as to closely reproduce the condition of a real electrode. Indeed, it is well known that carbon additives used to increase the electronic conductivity in the electrode can act as catalyst for the oxidative degradation of the electrolytes. The CV up to 5.0 V with PEO Pyr6 (ASW, green curves in top panel of Figure 4.11) shows a slight increase of the oxidation current with onset at about 3.5 V in the first cycle, which can be associated to the early FSI anion oxidation and decomposition on CC-Al. Notably, the oxidation current decreases with the number of cycles, suggesting that the passivation film formed on CC-Al can hinder the further oxidation of the electrolyte. On the other hand, PEO Pyr4 seems to undergo degradation, as suggested by increasing current density upon cycling. By looking at cathodic stability windows (CSW, bottom panels of Figure 4.11), the expected Na plating/stripping peak is missing, which would suggest high charge transfer resistance at the electrode/electrolyte interface [243–246]. However, the overall electrochemical stability windows result to be quite wide, ranging between ~ 0.5 -4.0 V. The ionic conductivity can be readily determined by electrochemical impedance spectroscopy (EIS) using symmetric cells with ion blocking electrodes (e.q., SS|membrane|SS configuration, SS = stainless steel, see Section 5.3.2 for technical details). The ionic conductivity is given by:

$$\sigma = \frac{d}{AR_b} \tag{4.5}$$

where d and A are geometrical parameters of the membrane, *i.e.*, thickness and area, respectively, and R_b is the bulk resistance. This value is extrapolated from the EIS experiment as the real part of the complex impedance signal (Z), which in the Nyquist plot ($-Z_{im}$ vs. Z_{re}) corresponds to a semicircle in the high-frequency range. The equivalent circuit for this configuration consists in the combination of R_b connected in series with the geometric capacitance. The so-obtained ionic conductivities are plotted against temperature in Figure 4.12a. The ionic conductivity plot of an extra polymer electrolyte (PEO_Pyr^{*}) is also reported (red curve), as it is explained further in the text.



Figure 4.12: a) Arrhenius plot of ionic conductivity, σ , as function of temperature, T, for PEO_Pyr4 (blue), PEO_Pyr6 (green) and PEO_Pyr* (red); b) PEO_Pyr6 film after conductivity measurement. The picture has been taken at GAME lab – Politecnico di Torino, where polymer materials have been prepared.

Transparency and flexibility of polymeric membranes are retained after conductivity measurements, as shown in Figure 4.12b, which confirms the thermal stability and mechanical integrity (leakage free) of the developed polymer electrolytes even after stress. Arrhenius-like dependence of ionic conductivity with temperature between -20 °C and 80 °C is detected for both electrolytes (blue and green curve in Figure 4.12). Ionic conductivity at RT is around $0.5 \,\mathrm{mS \, cm^{-1}}$, which is relatively high and comparable to similar materials reported in the literature [244, 245]. However, we have selected the PEO Pyr6 membrane for cell assembly because of: (i) the enhanced conductivity at each temperature owing to the higher amount of ionic liquid; (ii) the improved capability in forming a stable passivation film at the electrode/electrolyte interface upon oxidation (as discussed above, Figure 4.11). The HC CNC/PEO Pyr6 system has been assembled in a standard sandwich-like configuration, with the polymer membrane being interfaced to the disk electrode. The corresponding GC results are shown in left panel of Figure 4.13. The sandwich-like configuration only proceeds at low C-rate $(23.2 \,\mu A \, cm^{-2})$ and high temperature $(70 \,^{\circ}C)$. The cell exhibits quite high and stable Coulombic efficiency, but it barely delivers \sim 75 mA h g⁻¹, which is almost half the capacity of its liquid counterpart $(Pyr_{14}FSI:NaFSI, Figure 4.9c)$. To improve the cyclability at lower temperature, we have considered the extra PEO Pyr^{*} formulation with a RT-IL content equal to 70% wt. (highest possible amount to avoid compromising the mechanical integrity of the membrane), leading to an increase in ionic conductivity by an order of magnitude (up to ${\sim}5\,{\rm mS\,cm^{-1}}$

at RT, red curve in Figure 4.12a). This polymer electrolyte formulation has been prepared via *in situ* technique, which consists in the deposition of the precursor paste directly on top of the electrode disk, followed by the hot-pressing and UV-curing steps. In this way, the electrode/electrolyte surface contact is optimized thanks to the improved wetting of the active material particles, which likely results in enhanced utilization and diffusion at the interface and lower charge transfer resistance.



Figure 4.13: Galvanostatic cycling of HC-based Na metal cells with polymer electrolytes: a) Voltage vs. specific capacity profiles for selected cycles. The first charge/discharge cycle is shown in the inset; b) plots of specific charge capacity (red) and Coulombic efficiency (green) vs. cycle number.

Despite the lower capacity delivered in the GC runs with liquid electrolytes (Figure 4.9), HC_Coffee anode material has been preferred over HC_CNC for cell assembly owing to the higher Coulombic efficiency, which is crucial for stability in full cell configuration. The RT-GC run has been successfully recorded at C/50 C-rate $(1.1 \,\mu A \,\mathrm{cm^{-2}})$. The cell is shown to deliver $\sim 26 \,\mathrm{mA} \,\mathrm{hg^{-1}}$ reversible capacity (right panels in Figure 4.13). In situ prepared PEO_Pyr* has therefore been tested with NVPF. In this case, we have considered $65 \,\mathrm{mA} \,\mathrm{hg^{-1}}$ theoretical capacity corresponding to extraction of 1 equivalent of Na⁺ within 2.8-4.0 V. This voltage range is expected to be suitable to test solid polymer matrixes that are unstable at higher voltage values (see also ESW in Figure 4.11) and would undergo severe material degradation [246]. The resulting GC run performed at RT is reported in Figure 4.14.



Figure 4.14: Galvanostatic cycling of NVPF-based Na metal cell with in situ prepared PEO_Pyr* electrolyte: **a**) Voltage vs. specific capacity profiles for selected cycles. The first charge/discharge cycle is shown in the inset; **b**) plots of specific discharge capacity (blue) and Coulombic efficiency (green) vs. cycle number.

As it can be observed from Figure 4.14a, we have pushed the cut-off value up to 4.5 V from the 7th cycle, which did not jeopardize the test. We are actually able to identify the second plateau and achieve ~90 mA h g⁻¹ capacity. The direct deposition of the electrolyte paste onto the disk electrodes has effectively enabled the galvanostatic cycling of RT-IL/PEO with both HC and NVPF electrode materials in Na half-cells at room temperature. Our preliminary work unveils the promising performances of ternary electrolytes containing $Pyr_{14}FSI$ RT-IL, NaFSI salt and cross-linked PEO in lab-scale NIB devices and represents encouraging starting point to assess efficient configurations for future practical full-cell devices.

Further investigations are underway to improve the performance of these innovative electrolytes and understand their behavior in Na-based cells. On one hand, the application of polarizable MD simulations already assessed in RT-IL binary electrolytes (Section 4.1) can be extended to polymer based ones and assist the identification of key factors affecting ion transport also in ternary systems. On the other hand, the use of electrode materials with different morphologies (crystallinity, nanostructuring, porosity) may provide a more complete overview of electrolyte activity at interface, whereas supported by first-principles calculations. We aim to integrate both theoretical and experimental skills that have been acquired during the PhD course to pursue all these objectives and accomplish an in-depth comprehension of physico-chemical phenomena underlying the battery functioning.

5 Computational methods and experimental setup

In this chapter, the theoretical framework is presented in terms of both computational and experimental methodologies that have been adopted throughout the thesis work. *In silico* experiments concern either static and dynamics simulations (Sections 5.1 and 5.2, respectively), while experimental procedures concerning preparation, characterization and electrochemical tests of electrodes and electrolytes are described in Section 5.3.

5.1 Density Functional Theory

Quantum-mechanical calculations can be very helpful in shedding light on the batteries chemistry, which is based on charge and mass transport processes at heterogeneous materials interfaces. In the following, we present a brief overview of the general background and the specific strategies that have been adopted to investigate the structure-property relationship in the electrode materials of interest. At the foundation of Quantum Mechanics, there is the solution of the time-independent Schrödinger equation, which for a system of n electrons and N nuclei can be written as:

$$\hat{H}\Psi = \Psi E \tag{5.1}$$

where \hat{H} is the Hamiltonian, Ψ is the wave-function and E is the total energy. Analytical solution of Schrödinger equation is only possible for single electron systems, but the multi-particle problem can be solved numerically applying some approximation. The solutions can be generated without reference to experimental data (ab initio methods) or derived from atombased parameters (semi-empirical methods). The first step for simplifying the Schrödinger equation is the separation of electronic and nuclear degrees of freedom via the Born-Oppenheimer approximation: the electrons move much faster than nuclei because of their much lighter mass, so we can rule out the nuclear wave-function and solve only the electronic Schrödinger equation for each given nuclear configuration [247]. Focusing on the electronic structure problem, the term that makes the Schrödinger equation unsolvable for multi-electron systems is the electron-electron interaction term. The first approximation to this problem was to neglect this interaction and to build the wave-function as the product of atomic (or molecular) orbitals. The interaction between each electron and the other n-1 electrons is then recast into the Hamiltonian by a mean field approximation

(each electron moves in the average field generated by the all the other n-1 electrons), that is the Hartree-Fock (HF) theory [248]. HF theory is able to catch the 99% of the correct total energy of a given molecular system, but chemical reactions and main physico-chemical properties usually involve the missing 1% of that total energy. The difference between the true Energy and the HF solution is called correlation energy. Over last decades, several Molecular Orbital (MO) approaches have been built upon HF solutions in order to get the correlation energy via perturbation theory (e.q., MP2) or variational schemes (e.q., CI) [248]. These methods are usually referred to as post-HF and are able to achieve the so-called "chemical accuracy", but the high computational cost generally limits their use to small systems with few tens of atoms. The Density Functional Theory is an alternative theoretical framework used to solve the Schrödinger equation for many-electron systems [249]. The total energy of a system can be described as a functional of the electron density. In this way, a problem of 4N variables as in wave-function-based methods (3 spatial coordinates and 1 spin coordinate) can be solved with a real-space function with only 3 variables. For this reason, DFT-based methods are more suitable to model extended systems such as crystalline solids. However, the success of DFT strictly relies on the estimation of the functional form whose exact expression is unknown, as we are going to see in the next paragraphs. In 1927, Thomas and Fermi derived the kinetic energy for an electronic distribution, also called uniform gas model, as a function of the density, while the density itself is a function of the three-dimensional spatial coordinates. It was the first achievement towards DFT formalism: kinetic energy operator as density functional [249, 250]. In 1964, Hohenberg and Kohn set the rigorous foundation since they proved that the ground state density determines the external potential, and thus the Hamiltonian, and thus the wave-function (Hohenberg-Kohn Existence Theorem) [250, 251]. They also provided some indication on how to predict the density expression of a system, since density obeys a variational principle as wave-function within MO theory does (Hohenberg-Kohn Variational Theorem [250]). In 1965, Kohn and Sham proposed to solve the DFT problem considering the kinetic energy of non-interacting electrons, which lead to the same groundstate total density as some real and interacting system [252]. In this way, the energy functional expression becomes:

$$E[\rho(r)] = T[\rho(r)] + V_{ne}[\rho(r)] + V_{ee}[\rho(r)] + E_{XC}[\rho(r)]$$
(5.2)

where $T[\rho(r)]$ is the kinetic energy of non-interacting system, $V_{ne}[\rho(r)]$ is the external potential (electron-nucleus attraction), $V_{ee}[\rho(r)]$ is the Coulomb term (electron-electron repulsion) and $E_{XC}[\rho(r)]$ is the exchange-correlation functional. This last term contains the kinetic energy deriving from the interacting nature of electrons and all non-classical electron-electron interactions, that are the exchange and the correlation. All the unknown features of the density functional are retained by this E_{XC} term, which has become the target of interest for developing new and more accurate density functional models. In practice, in Kohn-Sham (KS) approach the pseudowave-function that minimizes $E[\rho(r)]$ also satisfies the pseudo-eigenvalue equation:

$$\left[-\frac{1}{2} \nabla_i^2 - \sum_j^N \frac{Z_j}{|r_i - r_j|} + \int \frac{\rho(r)}{|r_i - r|} + \frac{\delta E_{XC}}{\rho(r)} \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}) \quad (5.3)$$

where the KS one-electron operator is defined in bracket. Equation 5.3 would lead to the exact energy only if the exact form of the exchangecorrelation functional were known. So, even though DFT is in principle exact, the KS process must be carried out as an iterative Self Consistent Field (SCF) procedure to get an approximate solution. The functional dependence of E_{XC} on the electron density is expressed as an interaction between the electron density, $\rho(r)$ (per unit volume density), and an energy density, ε_{XC} (per particle density):

$$E_{XC} = \int \rho(r) \varepsilon_{XC}[\rho(r)] dr$$
(5.4)

where the energy density ε_{XC} is always treated as a sum of individual exchange and correlation contributions:

$$\varepsilon_{XC}[\rho] = \varepsilon_X[\rho] + \varepsilon_C[\rho] \tag{5.5}$$

Every approximation to E_{XC} aims to give an expression for the two terms in Equation 5.5. The Local Density Approximation (LDA) is the simplest one and considers a real and inhomogeneous system to be the sum of infinitesimal space volumes where we can think the electron density to be uniform and homogeneous as an electron gas. The value of ε_{XC} at some position r is computed from the value of ρ at that position, *i.e.*, the local value of ρ . However, in a molecular system the electron density is typically rather far from spatially uniform, while in solids it only can work for metals. One way to improve the E_{XC} functional is introducing the gradient of density, $\nabla \rho(r)$, *i.e.*, the Generalized Gradient Approximation (GGA). Most of GGA-functional expressions can be sum up as follows:

$$E_{X/C}^{GGA} = E_{X/C}^{LDA} - \sum_{\sigma} \int F(s_{\sigma}) \rho_{\sigma}^{4/3}(\vec{r}), d\vec{r}$$
(5.6)

where s_{σ} is called reduced density gradient, that is to be thought as a local inhomogeneity parameter, assuming large values either in regions of large or small densities:

$$s_{\sigma}(\vec{r}) = \frac{|\bigtriangledown \rho_{\sigma}(\vec{r})|}{\rho_{\sigma}^{4/3}(\vec{r})}$$
(5.7)

Nowadays several GGA functionals exist that can provide good accuracy with affordable computational cost (such as PBE, PW91 [253, 254]). We employ the PBE functional as it is one of the most used within GGA applied to extended systems. As shown in Equation 5.8, it has a very simple form and it is free of semi-empirical parameter:

$$F^{PBE} = \kappa - \frac{\kappa}{1 + \frac{\mu}{\kappa} s_{\sigma}^2} \tag{5.8}$$

with $\kappa = 0.804$ and $\mu = 0.21951$. In crystalline solids, a given set of atoms (a basis) is replicated periodically along the three dimensions of the real space, according to a given symmetry. The unit cell of a given crystal is a parallelepiped determined by three lattice vectors $(\vec{a}, \vec{b}, \vec{c})$ and three angles between them (α, β, γ) , containing the atomic basis. When replicated along x, y and z directions, the unit cell builds the entire infinite crystalline structure. The coordinates of atoms and any point in the unit cell are expressed in fractional coordinates of such cell vectors:

$$\vec{R} = \mu_a \vec{a} + \mu_b \vec{b} + \mu_c \vec{c} \qquad (\mu_a, \mu_b, \mu_c < 1) \tag{5.9}$$

In principle, a crystal contains an infinite number of atoms, and, hence, an infinite number of electrons. The Bloch theorem connects the properties of the electrons in a periodic system with those in the unit cell, leading to feasible electronic structure calculations in periodic solids [255]. The wave-function of an electron in an external periodic potential, U(r) = U(r+R), can be written as the product of a function with the same periodicity of the potential, $u_{\vec{k}}(\vec{r})$, and a purely imaginary phase factor arising from the translational symmetry, $e^{i\vec{k}\vec{r}}$:

$$\begin{split} \Psi_{\vec{k}}(\vec{r}) &= e^{i\vec{k}\vec{r}} u_{\vec{k}}(\vec{r}) \\ u_{\vec{k}}(\vec{r}) &= u_{\vec{k}}(\vec{r}+\vec{R}) \end{split} \tag{5.10}$$

Due to the periodicity of the potential, the periodic wave-function at any point of the crystal takes the form:

$$\Psi_{\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k}\cdot\vec{R}}\Psi_{\vec{k}}(\vec{r})$$
(5.11)

The phase factor, $e^{i\vec{k}\vec{R}}$, is called plane wave. From Equation 5.11, it can be seen that there is a particular class of vectors k (called K) for which the PW has the same periodicity of the crystal:

$$e^{i\vec{k}\vec{R}} = 1$$
 (5.12)

These vectors are called the reciprocal space. Analogously to Equation 5.9, any vector in the reciprocal space can be expressed in terms of three primitive vectors $(\vec{d}, \vec{e}, \vec{f})$:

$$\vec{K} = \mu_d \vec{d} + \mu_e \vec{e} + \mu_f \vec{f} \tag{5.13}$$

which are related to the real-space vectors as:

$$\vec{d} = 2\pi \frac{\vec{b} \times \vec{c}}{\Omega} \quad \vec{e} = 2\pi \frac{\vec{c} \times \vec{a}}{\Omega} \quad \vec{f} = 2\pi \frac{\vec{a} \times \vec{b}}{\Omega} \quad \Omega = \vec{a}(\vec{b} \times \vec{c}) \tag{5.14}$$

 Ω is the volume of the real-space unit cell. The K vector with μ_d = $\mu_e = \mu_f = 0$ is called Γ point. All wave-functions that obey periodic boundary conditions (PBC) stated by Equations 5.10 and 5.12 are repeated in every image of the unit cell in the real space, but also have the same value of K where $\mu_a, \mu_b, \mu_c < 1$, *i.e.* have a K-value confined in the unit cell of the reciprocal space, called Brillouin Zone (BZ). For this reason, the BZ contains all the information of the infinite crystal. In solid-state calculations, all the equations are solved within the BZ in the reciprocal space and so the number of electrons is limited to that contained in the unit cell. There are infinite K vectors in the BZ (Equation 5.13 with $\mu_a, \mu_b, \mu_c < 1$), but in practice only a finite number of k-points is selected (k-point sampling). A very popular truncation scheme is the one proposed by Monkhorst and Pack, that provides an equally spaced k-point mesh by performing $nd \times ne \times nf$ divisions along the d, e and f directions of the BZ [256]. The selection of k-points is not arbitrary and one must increase the number of k-points until the BZ is represented properly. The proper number of k-points depends on the volume of the unit cell (see Equation 5.14) and the nature of the chemical bond (in general, more delocalized systems require denser k-point meshes). For this reason, it is usually determined via energy convergence test on the given system. Oneelectron wave-functions can be expanded in terms of both localized and extended basis sets. The former are centered on the atomic nuclei (such as Gaussian-type orbitals, GTO) that are widely used for both molecular systems and condensed phases with PBC, while the latter are extended on the whole system and typically used in periodic calculations. A common choice is the PW basis set with the same periodicity of the cell, *i.e.*, whose wave vectors belong to the Brillouin zone:

$$\phi_{\vec{K}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{G}} e^{i\vec{G}\vec{K}}$$

$$\vec{G} = \mu_d \vec{d} + \mu_e \vec{e} + \mu_f \vec{f}$$
(5.15)

Expanding an unknown function in a set of known functions usually represents an approximation since the basis is never infinite. For plane waves, the basis set is limited to all plane waves with wave vector length smaller than some G_{max} value, *i.e.* confined within a sphere of radius G max and kinetic energy cutoff:

$$E_{cutoff} = \frac{\hbar^2 G_{max}^2}{2m} \tag{5.16}$$

The smaller the basis set size, the worse the representation of the wavefunction. On the other hand, a small basis set size is desired in terms of reduced computational effort. It is crucial to find the smallest basis set (smallest E_{cutoff}) necessary to expand the unknown wave-function with a certain level of accuracy. Energy cutoff, E_{cutoff} , is generally determined via energy convergence tests prior to any electronic structure calculations of a given system. One main drawback when using PW basis sets is that the number of PWs necessary to represent the inner states near the core is too large. A common practice is to adopt the pseudo-potential approach: core electrons are treated as frozen electrons that create a potential acting on the wave-functions associated to valence electrons (which are, instead, treated explicitly and expanded into a basis set). The potential function has the same shape of the true wave-function only outside the core region, beyond the so-called cutoff radius. The larger the cutoff radius, the fewer plane waves are needed. For a given atom, soft and hard pseudo-potentials differ for large and small cutoff radius, respectively. Popular pseudo-potentials used in solid-state calculations are Troullier-Martins [257], Ultrasoft [258], and Projector Augmented Wave [259] ones, which are the ones used in the VASP code. Some concerns may limit the reliability of DFT-based methods, for example in excited-state related properties, and further strategies are required, as discussed in the next paragraphs.

5.1.1 Self Interaction Error

One of the main issues in DFT is the so-called Self Interaction Error (SIE): the Coulomb term includes the interaction of an electron with itself, but this has no physical sense. This problem does not occur when the exchange term cancels the Coulomb term for i = j (as in HF calculations), while in DFT it is well marked for most localized electrons, *e.g.*, in d and f orbitals. SIE can be corrected through *a priori* approaches, by employing hybrid functionals that include a certain percentage of HF exchange in the E_{XC} term (*e.g.*, B3LYP, PBE0, HSE [260–263]). Equation 5.17 shows the explicit expression for the E_{XC} in the case of HSE functional:

$$E_{XC}^{HSE} = \frac{1}{4} E_X^{SR,HF}(\mu) + \frac{3}{4} E_X^{SR,PBE}(\mu) + E_X^{LR,PBE}(\mu) + E_C^{PBE} \quad (5.17)$$

where the 25% of HF exchange is computed only at short range, $E_X^{SR,HF}$, while all the other contributions are PBE-based for both short-range and long-range exchange, $E_X^{SR,PBE}$ and $E_X^{LR,PBE}$ respectively, and the correlation term, E_C^{PBE} . μ is called HF screening and stands for the SR/LR limit of separation. In particular, for HSE06 μ is equal to 0.2. Hybrid functionals are usually very expensive on extended materials, but can be useful for further refinement of electronic structure that only require single-point energy calculation on a given point of the potential energy surface. We use the HSE06 functional accordingly in some case studies (Sections 2.1 and 3.1). Otherwise, the *a posteriori* DFT+U scheme can be easily exploited for large systems with much lower computational effort [264]. In this case, the DFT energy is corrected for selected occupied orbitals on selected atoms, *e.g.* d orbitals in transition metals:

$$\varepsilon = \varepsilon^0 + (U - J)\left(\frac{1}{2} - n\right) \tag{5.18}$$

where n stands for occupied orbitals and (U - J) is an effective parameter that is applied to selected type of orbitals for selected atoms in the system. This term can be obtained either empirically (if experimental band gap is known) or *ab initio* (through energy convergence test on increasing-size clusters of such an element). PBE+U level of theory has been adopted for each material containing transition metals with open-shell electron populations (see Sections 2.1 and 3.1).

5.1.2 Dispersion forces

Another important issue in DFT concerns the inability to describe intraand inter-molecular dispersion interactions, also known as van der Waals forces. Dispersion forces are due to non-permanent dynamic perturbation of the electron density, while DFT is a ground-state theory. The electron densities of two different systems repel each other if they come too close. However, at intermediate distances, the electrons motion of one system induces slight perturbations in the electron density of the neighbor, leading to a temporary dipole moment that will induce an opposite charge polarization and thus creating a weak attractive force. This attraction decays with the inverse sixth power of the inter-molecular distance, but other contributions deriving from induced dipole-quadrupole, quadrupole-quadrupole interactions can be considered and vary as r^{-8}, r^{-10}, r^{-12} . In order to include non-covalent dispersion interactions in DFT-based description of any system, both a priori (vdW-based functionals) and a posteriori strategies exist, the latter being more convenient in terms of computational cost. The DFT-D approach developed by Grimme consists in adding a semi-empirical dispersion potential to the conventional Kohn-Sham DFT energy [265–267]. The total DFT-D3 energy is defined as:

$$E_{DFT-D3} = E_{KS-DFT} + E_{disp} \tag{5.19}$$

where the dispersion term, E_{disp} , is given by:

$$E_{disp}^{D3(BJ)} = -\frac{1}{2} \sum_{i \neq j} s_6 \frac{C_{6ij}}{r_{ij}^6} f_{d,6}(r_{ij}) + s_8 \frac{C_{8ij}}{r_{ij}^8} f_{d,8}(r_{ij})$$
(5.20)

In Equation 5.20, s_n is a scaling parameter that depends on the density functional, C_{nij} denotes the nth-order dispersion coefficient for the ij atom pair, r_{ij} is their inter-nuclear distance, and $f_{(d,n)}$ is a damping function that shut off the attractive term when the atom pair is at covalent bonding distances. One of the most used damping function is the Becke-Jonson (BJ) [266]:

$$f_{d,n}(r_{ij}) = \frac{s_n r_{ij}^n}{r_{ij}^n + (a_1 R_{0ij} + a_2)^n}$$
(5.21)

In DFT-D3, unlike in D2, the dispersion coefficients C_{6ij} are geometry dependent as they are adjusted on the basis of local coordination around atoms *i* and *j* and they are calculated from first principles. We employ the D3BJ correction when the vdW forces are expected to play an important role in determining the structural features in our systems (Sections 2.2 and 3.1).

5.1.3 Climbing-Image Nudged Elastic Band

The search for saddle points is a central problem in computational chemistry, since they correspond to the potential energy maxima along the MEP: once their energy is known, it is possible to calculate activation barriers of chemical reactions or, as in this case, diffusion events. This is why the relative distance along the MEP is a common choice for the reaction coordinate in the study of chemical mechanisms. The MEP is defined as the path between the initial and final state with the greatest statistical weight. The force acting on the atoms is only pointing along the path at any point and the energy is stationary for any perpendicular degree of freedom. In addition to the initial and final states, however, the MEP shows often more minima, corresponding to intermediate metastable configurations, which implicate an equal number of saddle points. This makes the aim more demanding, since it becomes necessary to have a good estimation of the MEP shape in order to identify the actual highest saddle point. Moreover, methods for finding saddle points must involve maximization of one degree of freedom and minimization of the others, since a first order saddle point is a maximum in one direction but a minimum in all the other. As a consequence, one of the main issues is developing a good and inexpensive way to identify the degree of freedom to maximize. The MEP is found by constructing a set of replicas of the system, called images, between the initial and final state. Every image is linked to the adjacent one with a spring interaction, in order to ensure continuity to the path. This way,

the total set of the images mimics the elastic band from which the method takes its name. An optimization of the forces acting on the band results in the optimization of the band itself, which reaches the MEP. An elastic band with N + 1 images can be denoted by $[R_0, R_1, R_2, ..., R_N]$, where R_0 and R_N are fixed and given by the energy minima corresponding to the initial and final state, while the other N-1 images are adjusted by the optimization algorithm. The characteristic feature of this method, which distinguishes it from other elastic band methods, is the presence of a force projection. It ensures both that the spring forces do not interfere with the convergence of the elastic band and that the true forces do not affect the distribution of the images along the MEP. Since only the parallel component of the spring force and the perpendicular component of the true force are taken into account, the tangent to the path must be estimated at each image and every iteration of the minimization, in order to decompose the forces in their components. Hence, the total force acting on an image is the sum of the spring force along the local tangent and the true force perpendicular to the local tangent:

$$F_i^{NEB} = F_i^{S\parallel} - F_i^{\perp} \tag{5.22}$$

where the true force is given by:

$$F_i^{\perp} = \nabla E(R_i) - \nabla E(R_i) \cdot \hat{\tau}_l \tag{5.23}$$

where E is the energy of the system as a function of all coordinates and $\hat{\tau}_l$ is the normalized local tangent at image *i*. The spring force is:

$$F_i^{S||} = k(|R_{i+1} - R_i| - |R_i - R_{i-1}|)\widehat{\eta}$$
(5.24)

where k is the spring constant. If it is the same for all the springs, the images converge to the MEP with equal spacing. The force projection is referred to as "nudging" because it avoids the true force-induced sliding of the band towards the minima, which lowers the density of the images in the high energy regions, where they are more needed. In addition, when the force projection scheme is not applied, the spring forces prevent the band to follow a curved MEP. So, the first advantage of the NEB method is the absence of competition between true and spring forces: the spring forces only control the spacing between the images. Their strength can be therefore varied of several orders of magnitude without affecting the equilibrium position of the band. The NEB method has disadvantage: even if the MEP is well approximated, the energy of the saddle point may be inaccurate because it has to be obtained by interpolation. This because it is not probable that an image lands exactly at or even near the saddle point. Consequently, when the energy barrier is narrow compared to the length of the MEP, the number of images reaching the neighborhood of the saddle point becomes small and the interpolation unsatisfying. To avoid this problem, a small modification, the Climbing Image Nudge Elastic Band method, has been implemented. This method enables to find saddle

points on the potential energy surface with the same efficiency reached for MEPs, but without extra significant computational cost. It consists in the identification of the image with the highest energy i_{max} after a few iterations with the regular NEB. This image, which takes the name of "climbing image", will then converge to the saddle point as long as the CI-NEB method converges. The remaining images in the band define the one degree of freedom for which the maximization must be carried out, as previously mentioned. The force on the climbing image is:

$$F_{i_{max}} = -\nabla E(R_{i_{max}}) + 2\nabla E(R_{i_{max}}) \cdot \widehat{\tau_{l_{max}}} \widehat{\tau_{l_{max}}}$$
(5.25)

This represents the full force due to the potential with the component along the elastic band inverted. From this equation it is clear that the maximum energy image is not affected by the spring forces. Therefore, the spacing of the images will be different on each side of the climbing image. As it moves up to the saddle point, the images on one side will get compressed and those on the other side spread out. A first advantage of CI-NEB method is that two or more climbing images can be easily identified if the MEP appears to have two or more high maxima close in energy. The only constraint is to have enough images near the climbing images to get a good approximation of the reaction coordinate, since this determines the climbing direction. In the neighborhood of the saddle point this approximation is granted by the fact itself that the band finally converges to the MEP. The most significant advantage of this method is that there is no additional cost in turning a certain image in the climbing one, since all the images are relaxed simultaneously. This appears relevant if compared with previous strategies doubling the computational cost, such as running a second elastic band between two images adjacent to the barrier in order to get a better estimate of the saddle point energy [76].

5.1.4 Computational details

Spin-polarized DFT calculations are performed with PAW potentials and PW basis sets, as implemented in the VASP code (version 5.4.4) [259, 268– 270]. We employ the PBE exchange-correlation functional within GGA. The DFT+U Hubbard-like correction scheme has been adopted to overcome the large SIE that affects DFT when applied to mid-to-late first row TM with tightly localized d electrons ($U_{eff} = 3.3$ eV for Ti [271], see Section 2.1; $U_{eff} = 4.0$ eV for both Ni and Mn atoms [272] (Section 3.1). The D3-BJ dispersion correction is added to account for van der Waals (vdW) interactions that play a crucial role at interface (Section 2.2) and layered structures (Section 3.1) [265–267]. Dipole corrections are applied when slab approach has been considered (Sections 2.1 and 2.2) to avoid long-range polarization from the periodic images along the c-direction [273]. CI-NEB method is employed to determine MEPs of Na migration and corresponding energy barrier heights in TiO₂ and MoS₂/Graphene systems (Sections 2.1 and 2.2, respectively) [76]. Kinetic energy cutoff and k-points sampling schemes are determined via convergence tests to ensure converged energies within 3meV/f.u. (600 eV and Monkhorst-Pack based $2x2x1 \ k$ -points sampling for TiO₂ (Section 2.1); 600 eV and Γ -centered $4x4x1 \ k$ -points sampling for MoS₂/Graphene (Section 2.2); 750 eV and Γ -centered $4x4x4 \ k$ -points sampling for NNMO (Section 3.1)). Lattice constants and atomic positions are relaxed until the maximum forces acting on each atom were below $0.03 \text{ eV } \text{Å}^{-1}$. Convergence threshold for energy is set to 10^{-5} eV . Electronic structure related properties (*e.g.*, PDOS, magnetization, Bader charges, CD plot) are obtained as single-shot calculations on minimumenergy structures.

5.2 Molecular Dynamics

Electronic structure methods, such as DFT, are typically used for solving the Schrödinger equation in a small portion of the potential energy surface (PES) of a given system. In fact, locating minima and saddle points corresponds to modeling the system at a temperature of 0 K, where all molecules are in their ground electronic, vibrational and rotational states. Just as zero-point vibration introduces probabilistic weightings to single-molecule structures, so too thermodynamics dictates that, given a large collection of molecules, probabilistic distributions of structures will be found about different local minima on the PES at non-zero absolute temperatures. The relative probability of clustering about any given minimum is a function of the temperature and some particular thermodynamic variables characterizing the system. Those variables being held constant define the ensemble. There are two major techniques for generating an ensemble and, for instance, incorporate the effect of finite temperature in the simulation process: Monte Carlo and molecular dynamics. These methods are capable of reproducing the aspects of molecular behavior by sampling the phase space, the 6N-dimensional space defined by positions, q, and momenta, p, of each particle. At any instant in time, the system occupies one point in phase space (X) and the collection of all these points is called trajectory:

$$X = (x_1, y_1, z_1, p_{x,1}, p_{y,1}, p_{z,1}, x_2, y_2, z_2, p_{x,2}, p_{y,2}, p_{z,2}, ...)$$

$$q = (x_1, y_1, z_1, x_2, y_2, z_2, ...)$$

$$p = (p_{x,1}, p_{y,1}, p_{z,1}, p_{x,2}, p_{y,2}, p_{z,2}, ...)$$

$$X = (q, p)$$
(5.26)

5.2.1 Solving the dynamical equation

In Monte Carlo (MC) methods, a sequence of points in phase space is generated from an initial geometry by adding a random "kick" to the coordinates of a randomly chosen particle (atom or molecule). The new configuration is accepted if the energy decreases and with a probability of $e^{-\Delta E/kT}$ if the energy increases. MC simulations require only the ability to evaluate the energy of the system, which may be advantageous if calculating the first derivative is difficult or time-consuming. Furthermore, since only a single

particle is moved in each step, only the energy changes associated with this move must be calculated, not the total energy for the whole system. A disadvantage of MC methods is the lack of the time dimension and atomic velocities, and they are therefore not suitable for studying time-dependent phenomena or properties depending on momentum. Molecular Dynamics (MD) methods generate a series of time-correlated points in phase space (a trajectory) by propagating a starting set of coordinates and velocities according to Newton's second equation by a series of finite time steps. MD simulations implicitly have both atomic velocities and time dependence, and are thus suitable for modeling for example transport phenomena and diffusion. Running an MD simulation requires the ability to calculate the force (first derivative of the energy) on all particles in the system in addition to the energy. For parameterized energy functions, such as those used in force field methods, this is not a limitation as forces can be calculated almost as easily as the energy. Furthermore, since all particles are moved in each step, the whole energy function (and gradient) must be recomputed at each step. A simulation can be characterized by quantities such as volume (V), pressure (P), total energy (E), temperature (T), number of particles (N), chemical potential (μ) , etc., but not all of these are independent. For a constant number of particles, either the volume or the pressure can be fixed, but not both. Similarly, either the total energy or the temperature can be fixed, but not both, and a constant chemical potential is incommensurable with a constant number of particles. The ensemble is labelled according to the fixed quantities (e.q., the NVT) is the canonical

ensemble where number of particles, volume and temperature are fixed; the micro-canonical NVE ensemble has fixed number of particles, volume and energy; NPT is the isothermal-isobaric ensemble with fixed number of particles, pressure and temperature; etc..), with the remainder being derived from the simulation data, and thus displaying a statistical fluctuation. At a finite temperature, the average kinetic energy is directly related to the temperature and the molecule(s) explores a part of the surface with energies lower than the typical kinetic energy. One possible way of simulating the behavior at a finite temperature is by allowing the system to evolve according to the relevant dynamical equation. For nuclei, this is normally Newton's second law, although the (nuclear) Schrödinger equation must be used for including quantum effects, such as zero point vibrational energy and tunneling. A dynamics simulation is also required if the interest is in studying time-dependent phenomena, such as transport, and the results of a simulation can yield information about the spectral properties, such as the IR spectrum. A dynamics simulation requires a set of initial coordinates and velocities, and an interaction potential (energy function). For a short time step, the interaction may be considered constant, allowing a set of updated positions and velocities to be estimated, at which point the new interaction can be calculated. By taking a (large) number of (small) time steps, the time behavior of the system can be obtained. Since the phase space is huge, and the fundamental time step is short, the simulation will only explore the region close to the starting point, and several

different simulations with different starting conditions are required for estimating the stability of the results. Nuclei are heavy enough that they, to a good approximation, behave as classical particles and the dynamics can thus be simulated by solving Newton's second equation, F = ma, which in differential form can be written as:

$$-\frac{dV}{dr} = m\frac{d^2r}{dt^2} \tag{5.27}$$

where V is the potential energy at position r. The vector r contains the coordinates for all the particles, *i.e.*, in Cartesian coordinates it is a vector of length $3N_{atom}$. The left-hand side is the negative of the energy gradient, *i.e.*, the force (F) on the particle(s). Given a set of particles with positions r_i , the positions a small time step Δt later are given by a Taylor expansion:

$$r_{i+1} = r_i + \frac{\partial r}{\partial t} (\Delta t) + \frac{1}{2} \frac{\partial^2 r}{\partial t^2} (\Delta t)^2 + \frac{1}{6} \frac{\partial^3 r}{\partial t^3} (\Delta t)^3 + \dots$$

$$r_{i+1} = r_i + v_i (\Delta t) + \frac{1}{2} a_i (\Delta t)^2 + \frac{1}{6} b_i (\Delta t)^3 + \dots$$
(5.28)

The velocities v_i are the first derivatives of the positions with respect to time at time t_i , the accelerations a_i are the second derivatives at time t_i , the hyper-accelerations b_i are the third derivatives, and so on. The positions a small time step Δt earlier are derived from Equation 5.28 by substituting Δt with $-\Delta t$:

$$r_{i-1} = r_i - v_i(\Delta t) + \frac{1}{2}a_i(\Delta t)^2 - \frac{1}{6}b_i(\Delta t)^3 + \dots$$
 (5.29)

Addition of Equations 5.28 and 5.29 gives a recipe for predicting the position a time step Δt later from the current and previous positions, and the current acceleration. The latter can be calculated from the force, or equivalently, the potential.

$$r_{i+1} = (2r_i - r_{i-1}) + a_i(\Delta t)^2 + \dots$$
(5.30)

This is the Verlet algorithm for solving Newton's equation numerically [274]. At each time step, the acceleration must be evaluated from the forces, which then allows the atomic positions to be propagated in time and thus generate a trajectory. As the step size Δt is decreased, the trajectory becomes a better approximation to the "true" trajectory, until the practical problems of finite numerical accuracy arise (the forces cannot be calculated with infinite precision). A small time step, however, means that more steps are necessary for propagating the system a given total time, *i.e.*, the computational effort increases inversely with the size of the time step. There are two main drawbacks when using Verlet algorithm: the first one is numerical, since the new positions are obtained by adding a small number (the term proportional to Δt^2) to the difference between two large numbers $(2r_i - r_{i-1})$ which may lead to truncation errors due to finite precision; on the other hand, velocities do not appear explicitly, which is a problem for generating ensembles at constant temperature. Both limitations can be overcome by employing the leap-frog algorithm [275]. Performing expansions analogous to Equations 5.28 and 5.29 with half a time step followed by subtraction gives:

$$r_{i+1} = r_i + v_{i+\frac{1}{2}} \Delta t \tag{5.31}$$

The velocity is obtained by analogous expansions:

$$v_{i+\frac{1}{2}} = v_{i-\frac{1}{2}} + a_i \Delta t \tag{5.32}$$

The explicit presence of velocities facilitates the coupling to an external heat bath, making the leap-frog algorithm more suitable when temperature is fixed. Here, the disadvantage is that the positions and velocities are not known at the same time, as they are always out of phase by half a time step. The latter abnormality can be removed by the velocity Verlet algorithm [276]:

$$r_{i+1} = r_i + v_i \Delta t + \frac{1}{2} a_i \Delta t^2$$

$$v_{i+1} = v_i + \frac{1}{2} (a_i + a_{i+1}) \Delta t$$
(5.33)

The time step employed is an important control parameter for a simulation. The maximum time step that can be taken is determined by the rate of the fastest process in the system, *i.e.*, typically an order of magnitude smaller than the fastest process. Molecular motions (rotations and vibrations) typically occur with frequencies in the range of 10^{11} - 10^{14} s⁻¹

(corresponding to wave-numbers of 3 to $3300 \,\mathrm{cm}^{-1}$), and time steps of the order of femtoseconds (10^{-15} s) or less are required to model such motions with sufficient accuracy. This means that a total simulation time of 1 ns requires $\sim 10^6$ time steps, and 1 µs requires $\sim 10^9$ time steps. A million time steps is already a significant computational effort and typical simulation times are in the nano or picosecond range. Unfortunately, many interesting phenomena occur on a substantially longer time scale: protein folding and chemical reactions, for example, occur on the order of milliseconds or seconds. Furthermore, a single trajectory may not be adequate for representing the dynamics, thus requiring that many runs must be carried out with different starting conditions (positions and velocities) and be properly averaged. For molecules, the fastest processes are the stretching vibrations, especially those involving hydrogen, the lightest atom. These degrees of freedom have relatively little influence on many properties, and thus it is advantageous to freeze all bond lengths involving hydrogen atoms. This strategy would allow longer time steps to be taken, and consequently longer simulation times to be obtained for the same computational cost. As all atoms move individually according to Newton's equation, constraints must be applied for keeping bond lengths fixed. This is normally done for example by means of the SHAKE algorithm [277, 278]. Enforcement of bond length constraints typically allows the time step to be increased by a factor of 2 or 3. Angle constraints may also be used in principle, but it is much less frequent since angle bending can affect calculated properties more than bond stretching. A standard MD simulation generates an NVE ensemble, *i.e.*, the temperature and pressure will fluctuate. The total energy is a sum of the kinetic and potential energies, and can be calculated from the positions and velocities.

$$E_{tot} = \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2 + V(r)$$
(5.34)

Owing to the finite precision with which the atomic forces are evaluated, and the finite time step used, the total energy is not exactly constant, but this error can be controlled by the magnitude of the time step. Indeed, preservation of the energy to within a given threshold may be used to define the maximum permissible time step. The temperature of the system is proportional to the average kinetic energy:

$$\langle E_{kin} \rangle = \frac{1}{2} (3N_{atoms} - N_{constraint})kT$$
 (5.35)

The number of constraints is typically three, corresponding to conservation of linear momentum. Note that for 1 mole of particles, Equation 5.35 reduces to the familiar expression $\langle E_{kin} \rangle = \frac{3}{2}RT$. Since the kinetic energy is the difference between the total energy (almost constant) and the potential energy (depends on the positions), the kinetic energy will vary significantly, *i.e.*, the temperature will be calculated as an average value with an associated fluctuation. Similarly, if the volume of the system is fixed, the pressure will fluctuate. Although the *NVE* is the natural ensemble generated by an MD simulation, it is possible to generate *NVT* or *NPT* ensembles by modifying the velocities or positions in each time step. The system may be coupled to a "heat bath", which gradually adds or removes energy to/from the system with a suitable time constant, often called a thermostat. The kinetic energy of the system is again modified by scaling the velocities (v_{sf} is the velocity scale factor), but the rate of heat transfer is controlled by a coupling parameter τ :

$$\frac{dT}{dt} = \frac{1}{\tau} (T_{desired} - T_{actual}) \Leftrightarrow v_{sf} = \sqrt{1 + \frac{\Delta t}{\tau} (\frac{T_{desired}}{T_{actual}} - 1)}$$
(5.36)

The pressure can similarly be held (approximately) constant by coupling to a "pressure bath". Instead of changing the velocities of the particles, the volume of the system is changed by scaling all coordinates according to:

$$\frac{dP}{dt} = \frac{1}{\tau} (P_{desired} - P_{actual}) \Leftrightarrow c_{sf} = \sqrt[3]{1 + \kappa \frac{\Delta t}{\tau} (\frac{P_{actual}}{P_{desired}})}$$
(5.37)

Here the constant κ is the compressibility of the system. Thermostat and barostat methods are widely used but again do not produce a canonical ensemble. They do produce correct averages but give incorrect fluctuations of properties. In Nosé-Hoover methods the heat and pressure baths are considered an integral part of the system and assigned fictive dynamic variables, which are evolved on an equal footing with the other variables [279, 280].
5.2.2 Molecular Mechanics

One way to easily compute the forces required to solve Newton equation of motion (Equation 5.27) is provided by Molecular Mechanics (MM). If it can be assumed that only classical physics applies on the given chemical system, hence it is possible to define a force field:

$$E_{tot} = \sum_{ij}^{bonds} \frac{k_{r,ij}}{2} (r_{ij} - r_{0,ij})^2 + \sum_{ijk}^{angles} \frac{k_{\theta,ijk}}{2} (\theta_{ijk} - \theta_{0,ijk})^2 + + \sum_{ijkl}^{dihedrals} \sum_{m=1}^{4} \frac{V_{m,ijkl}}{2} + [1 + (-1)^m \cos(m\varphi_{ijkl})] + + \sum_{i}^{atoms} \sum_{j \neq i} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$$
(5.38)

where the total (steric) energy of a molecule is expressed in terms of several contributions, provided that the constituting nuclei are considered as hard spheres with only classical forces acting among them. The first energy term is the bond stretching contribution and has the form of the Hooke's law for a spring, where k is the force constant of the spring, *i.e.*, the bond strength. The second energy contribution refers to valence angle bending. These functional forms for bond stretching and bending works well close to equilibrium. For instance, in some force fields bond stretching is evaluated by including additional anharmonic terms or the Morse function. Torsions also have a remarkable contribution to the steric energy of a molecule. The convention is to define the torsion angle as positive if one must rotate

the bond in front of the bisecting plane in a clockwise fashion to eclipse the bond behind the bisecting plane. As the minimum energy for many torsions is for the anti-periplanar arrangement (*i.e.*, $\omega = \pi$), ω values are often taken in the range between $-\pi$ and π . Since the torsion angle itself is periodic, so has to be the corresponding potential energy. This is frequently expressed as an expansion of periodic functions, e.g., a Fourier series (third energy term in Equation 5.38). The factor of 1/2 is included so that the term amplitude V_m is equal to the maximum the particular term can contribute to E_{tot} . The factor of $(-1)^m$ is included so that the function in brackets within the sum is zero for all m when $\omega = \pi$. The last term is related to non-bonding interactions, *i.e.*, Lennard-Jones and Coulombic potential for taking into account dispersion and electrostatic contributions. It is noteworthy that all the parameters shown in Equation 5.38 depend on specific pair or triplet of atoms. Determining the values that are suitable to represent a given chemical system constitutes the parametrization of the desired force field and is key when using MM.

5.2.3 Simulation details

In this paragraph, we have collected all the simulation details that have been employed to perform MD to study sodium transport in RT-IL based electrolytes (see Section 4).

Force field. We used the CL&Pol force field for ionic liquids [209, 213], which is a polarizable version of the widely adopted CL&P fixed-charges

model [207, 208]. The CL&Pol force field uses Drude induced dipoles [281] which, placed on each atomic site, represent the induction effects. The induced dipoles are formed by an additional point charge, the Drude particle (DP), and its opposite charge, the Drude core (DC), placed on the atom. The DP and DC are linked by a harmonic bond of equilibrium length 0 and the Coulomb interactions between each DC and its DP are excluded from computation of energies and forces. The DP carries a charge q_D and the DC a charge $q - q_D$, where q is the total charge of the atom. The extension of the harmonic springs allows the Drude dipoles to respond to the local electric field. We followed the approach of Lamoureux and Roux [282] in assuming a global force constant of $k_D = 4184 \,\mathrm{kJ \, mol^{-1} \, \AA^{-2}}$ for the DC–DP bonds and determining q_D values from the atomic polarizabilities, $\alpha = q_D^2/k_D$. We adopted induced dipoles with a positive charge q_D on the DP, which enables more robust trajectories in the presence of the high positive charge density on the Na ion. In our systems, negative Drude particles would create more risks of a polarization catastrophe, with Drude particles being pulled too far away from their cores. Thole damping functions [283, 284] were employed to reduce at short range the electrostatic interactions between induced dipoles, in order to avoid excessive correlation between neighboring DP. A universal value of the parameter a = 2.6 was chosen, in accord with the functional form given in the literature [283, 285]. The force field parameters necessary to take into account polarization effects were obtained from *ab initio* calculations of induction

(polarization) and dispersion energies, using symmetry-adapted perturbation theory (SAPT) [213]. These detailed calculations were performed for a set of molecular fragments including common cation and anion headgroups, side chains and molecular solvents. The systems considered here were built from those fragments, namely Pyr_{13}^{+} was represented by the cation head group, $C_1C_1pyr^+$, with sites in the alkyl chain derived from the C_4H_{10} fragment. With polarization being taken into account explicitly by the Drude induced dipoles, the CL&Pol model uses van der Waals (or Lennard-Jones) parameters from original (non-polarizable) CL&P model, rescaled on the basis of the relative contributions of dispersion and induction energies obtained from SAPT. In this manner, in the polarizable force field the Lennard-Jones potential terms account only for repulsive and dispersive interactions, and not for induction implicitly. The k-factors [213] used here to obtain the Lennard-Jones terms in the polarizable force field are fragment-based and have the following values: k(pyr-FSI) = 0.54, $k(\text{pyr-CC}) = 0.67, \ k(\text{FSI-CC}) = 0.77, \text{ where CC stands for the C}\beta$ and $C\gamma$ atoms (and respective H atoms) in the alkyl side chain of the pyrrolidinium cation. The parameters for sodium were taken from a polarizable model from the literature [286] that uses Drude induced dipoles. In all, the additional information at the molecular level required to parameterize a polarizable force field (from a fixed-charge one) are the relative weight of induction versus dispersion terms, obtained from SAPT calculations, and atomic polarizabilities, which we took from the recent literature [286, 287]. In order to set up non-polarizable simulations for comparison, we modified the electrostatic contribution in the CL&P force field by scaling down the atomic charges by a factor of 0.8 [210], which is a simple fix that improves calculation of transport properties (at the cost of worsening the density values and structural quantities).

Molecular dynamics simulations. Drude induced dipoles have been implemented in major molecular dynamics codes, including the LAMMPS code [283, 288], which we used for the present simulations. The additional degrees of freedom corresponding to the relative motion of the DP with respect to their cores are handled by a separate thermostat in order to keep these modes at very low temperature [282, 283], thus closely matching the trajectories of relaxed induced dipoles. We built 5 simulation boxes containing 216 ion pairs for the mixed NaFSI-Pyr $_{\rm 13}{\rm FSI}$ system, with a series of salt concentrations (x_{NaFSI} of 0.0, 0.1, 0.3, 0.5 and 0.9, with x denoting mole fraction). Initial configurations were generated using the fftool [289] and packmol [290] utilities. A cutoff distance of 12 Å was considered for the Lennard-Jones potential and for the real-space part of electrostatics. The particle-particle particle-mesh method was used to evaluate electrostatic energies with an accuracy of 10^{-4} . Hydrogen-terminating bonds were constrained using the SHAKE algorithm [277, 278]. The time step was set to 1 fs. After initial 0.5 ns equilibration runs, we collected 8 ns NPTtrajectories, regulated by Nosé-Hoover thermostat and barostat [279, 280], with temperature being set at 353 K and pressure at 1 bar, for comparison with experimental data from the literature [215]. The shear viscosity was computed for all the systems from non-equilibrium MD trajectories

using the periodic perturbation method [221] by applying a cosine-shaped acceleration along the x-axis with periodicity along the z-axis:

$$\eta = \frac{\mathcal{A}}{\mathcal{V}} \frac{l_z^2 \rho}{4\pi^2} \tag{5.39}$$

where \mathcal{A} is the amplitude of imposed acceleration, l_z is the height of the box and \mathcal{V} is the amplitude of the generated velocity profile. We use the temperature-grouped dual-Nosé-Hoover thermostat which enables correct equipartition of kinetic energy among unconstrained degree of freedom [291].

5.3 Experimental section

This Section aims to collect all the experimental procedures and techniques that have been adopted for the physico-chemical characterization of salt/RT-IL solutions (Section 4.1) and the electrochemical tests on Na-based cells (Section 4.2).

5.3.1 Physico-chemical characterization of sodium salt/RT-IL solutions

Materials. The N,N-methyl propyl pyrrolidinium bis(fluorosulfonyl)imide (Pyr₁₃FSI) RT-IL was purchased from Solvionic 99.5 % pure. The ionic liquid was degassed under primary vacuum for 48 h and was kept dried

and degassed inside a glove box (Jacomex GP Campus) before sample preparation. Sodium bis(fluorosulfonyl)imide (NaFSI) was purchased from Solvionic 99.7 % pure. Before utilization, the salt was kept inside the glove box and used without further treatment. Deuterated chloroform (CDCl₃) 99.80 % for NMR, was purchased from Eurisotop with a water content below 0.01 %.

Sample preparation. $Pyr_{13}FSI:NaFSI solutions were prepared inside$ the glove box at room temperature by weighing the components using a $New Classic MS Mettler Toledo balance with an accuracy of <math>\pm 0.01$ mg and shaking by hand the flask for 5 to 10 min. To record the NMR spectra, the samples were placed in NMR tubes and degassed under primary vacuum for over 1 h before each measurement. The NMR spectra of the pure ionic liquid and of $Pyr_{13}FSI:NaFSI$ solutions were carried out using CDCl₃. To avoid changes in composition, an inner coaxial tube (5 mm diameter) containing the deuterated solvent was used. The same inner tube was used with all the samples in order to avoid spectral differences due to the magnetic susceptibility of the material.

Table 5.1: Salt and RT-IL masses, m(g), and molar fractions, x, of $Pyr_{1s}FSI:NaFSI$ solutions with corresponding uncertainties.

$\mathbf{m}_{\mathrm{NaFSI}}$	${ m m}_{ m Pyr}{ m _{13}FSI}$	x	
0.24625 ± 0.00008	3.34916 ± 0.00007	0.10034 ± 0.00003	
0.94658 ± 0.00002	3.35114 ± 0.00008	0.29994 ± 0.00001	
2.19761 ± 0.00002	3.39323 ± 0.00003	0.49555 ± 0.00001	

Density and viscosity measurements. Density and viscosity were measured in a coupled Anton Paar densimeter (DMA 5000 M) and viscometer (LOVIS 2000 ME). In the densimeter, a U-shaped vibrating-tube is electronically excited at its characteristic frequency, which depends on the density of the sample inside. Calibration of the instrument was performed using two substances of precisely known densities: air and ultra-pure water (density standard provided by Anton Paar). The precision and accuracy of the measurements are $5 \times 10^{-6} \,\mathrm{g \, cm^{-3}}$ and $7 \times 10^{-6} \,\mathrm{g \, cm^{-3}}$, respectively, in density and 0.01 °C in temperature. The viscometer is based on the Hoeppler falling ball principle, according to which the rolling time of a ball through the liquid confined in a glass capillary is determined. In order to cover the viscosity range of our samples in the working temperature range, two capillaries with different diameters, 1.8 mm and 2.5 mm, and two balls of the same material, were calibrated with two different standard oils, APN26 and APN415, respectively. The precision and accuracy of the measurements are 0.05 and 0.5%, respectively, in viscosity and 0.02 °C in temperature. Both the densimeter and viscometer cells were filled with ca. 1 mL of sample and the measurements carried out simultaneously, using the temperature-table scan mode at atmospheric pressure and in the temperature range 293.15 to 353.15 K.

NMR experiments. NMR experiments were carried out on a Bruker Avance 400 MHz spectrometer equipped with a diffusion probe BBdiff with Z gradients up to $2.8 \,\mathrm{Tm}^{-1}$ at 10 Å. The self-diffusion coefficients of the species in each sample were determined through ¹H and ¹⁹F pulsed-fieldgradient spin-echo NMR experiments (PFGSE), using a bipolar-pulse longitudinal eddy current delay (BBPLED) pulse sequence. The temperature was regulated at 298 K and a coaxial insert containing the deuterated solvent was used to lock and adjust the chemical shift scale. For each PFGSE experiment, the pulse gradient and diffusion time were optimized in order to get a signal attenuation of about 95%. The relaxation delay was set to 1.5 s and 8 scans were acquired for each measurement. Rectangular pulse field gradients shaped with smoothed edges (SMSQ10.100) were used with a length δ going from 0.8 to 2.5 ms for ¹H experiments and from 1.5 to 2.5 ms for ¹⁹F experiments. The intensity of the gradient was linearly incremented from 5.26 to 258.06 G cm⁻¹ for ¹H-NMR experiments and from 3.72 to 182.50 G cm⁻¹ for ¹⁹F-NMR ones. Data were processed using the Topspin v3.6 software and diffusion curves were fitted using DynamicsCenter, implemented in Topspin.

5.3.2 Electrochemical characterization of RT-IL/PEO based electrolytes

Electrolytes preparation. Preparation of electrolyte samples has been carried out in an Ar-filled dry glovebox (Jacomex GP2 concept, $O_2 < 5$

ppm, $H_2O < 1$ ppm). Two liquid electrolytes have been prepared by mixing a RT-IL with a sodium salt under stirring: N,N-methylbuthyl pyrrolidinium bis (fluorosulfonyl)imide (Pyr₁₄FSI) and 1-ethyl 3-methyl imidazolium bis (fluorosulfonyl)imide (EmiFSI) have been mixed with sodium bis (fluorosulfonyl)imide salt (NaFSI) at 6:1 molar ratio (Battery grade, Solvionic, RT-ILs used as received, NaFSI dried under vacuum at 70°C overnight). Composition is reported in Table 5.2.

Table 5.2: Composition of liquid electrolytes, expressed in weight percentage, wt. (%).

sample	RT-IL	salt	
$Pyr_{14}FSI:NaFSI$	90.5	9.5	
EmiFSI:NaFSI	89.6	10.4	

Pyr14FSI:NaFSI has been chosen over EmiFSI:NaFSI for implementation in poly(ethylene oxide) (PEO) membranes, as detailed in Section 4.2. Polymer electrolytes have been prepared by adding benzophenone (BP, Sigma-Aldrich, used as received, 0.05% wt. of PEO mass) and then PEO (M_n 200000 Da, Sigma-Aldrich, vacuum-dried at 55 °C for 48 h) stepwise into two RT-IL/salt solutions with different concentration, *i.e.*, 6:1 and 4:1 molar ratio, on a hot plate at 70 °C under constant stirring. The mixtures have been hand-ground and reheated at 70 °C on a hot plate for 1 h. The final compositions are reported in Table 5.3. The extra PEO_Pyr* formulation has been considered to improve the cyclability of this kind of electrolytes in lab-scale Na metal cells, as detailed in Section 4.2. For all the formulations, the EO:Na molar ratio is kept constant and equal to 20, while the RT-IL/salt one varies from 6 in PEO_Pyr6 to 4 in PEO_Pyr4 and reaching 70%wt. in PEO_Pyr*. The samples have been placed between two poly(ethylene terephthalate) (PET, Mylar) sheets and sealed inside a poly(propylene) (PP) bag. The resulting pastes have been hot-pressed at 8 bar and 70 °C for 15 min and then cross-linked for 3 min per side under UV light (UV-curing) using a medium pressure Hg lamp (Helios Quartz). The films have then been peeled off from the PET foils in a dry room (10 m^2 , R. H. $< 2\% \pm 1$ at 20 °C produced by Soimar Group).

Table 5.3: Composition of polymer electrolytes, expressed in weight percentage, wt. (%), for each component, i.e., RT-IL, salt, PEO and BP.

sample	RT-IL	salt	PEO	BP
PEO_Pyr4	53.36	8.41	36.41	1.82
PEO_Pyr6	63.11	6.66	28.80	1.43
PEO_Pyr*	70.03	10.91	18.15	0.91

Electrochemical impedance spectroscopy. The ionic conductivity has been obtained from electrochemical impedance spectroscopy (EIS, freq. range 300 kHz - 1 Hz, VAC = 20 mV) on a VMP3 workstation (Biologic), using stainless steel (SS) electrodes in symmetric SS|PEO_Pyr|SS ECC-Std cells (EL-cell, Germany). The spectra have been collected at 10 °C intervals between -20 °C and 80 °C, inside an environmental simulation chamber (MK-53, Binder), with 90 min equilibration time at each step. Polymer electrolytes have been cut into disks with an area of 2.54 cm^2 . Cyclic voltammetry. The electrochemical stability window (ESW) has been evaluated at room temperature by means of cyclic voltammetry (CV) in two-electrodes configuration, with the electrolytes assembled with carboncoated aluminum and Na metal anode in ECC-Std cells (EL-cell, Germany). The CV measurements have been performed at a scan rate of 0.1 mV s^{-1} within the following voltage ranges: -0.5 to 3 V vs. Na for cathodic (CSW) and 2.5 to 5 V vs. Na for anodic (ASW) stability windows. Both electrodes and polymer electrolytes have been cut into disks with an area of 2.54 cm^2 .

Electrodes preparation. A slurry of 2% wt. polyvinylidene fluoride (PVdF, Solef 1010) in N-Methyl-2-pyrrolidone (NMP) has been prepared. Acetylene black (CB) has been added as electron conductor together with HC/NVPF as active materials, leading to 70:20:10 (HC:CB:PVdF) and 80:10:10 (NVPF:CB:PVdF) compositions (given in weight percentage). In all cases, the obtained dispersion has been deposited onto aluminum current collector foils with doctor blade technique and then dried in air. The resulting electrodes (\emptyset = 18 mm) have a HC/NVPF mass loading of 0.28/0.31 mg cm⁻².

Cell assembly and Galvanostatic cycling. Na metal from Sigma Aldrich has been used for the disk electrodes. The cells with liquid/polymer electrolytes have been assembled in the Ar-filled dry glovebox in ECC-Std cells (EL-cell, Germany) with a 16 mm Na metal disk in a two-electrodes configuration. For liquid electrolytes, a glass wool Whatman separator drenched with 200 µl of solution is employed. All the cells have

been galvanostatically cycled (GC) with an Arbin BT2000 battery tester at ~ 4.4-4.8 μ A cm⁻². Specific capacity has been calculated with respect to the active material (HC/NVPF) content. Cut-off voltage and cycling temperature varied as declared in the figures and related discussion.

6 Conclusions and Perspectives

A general overview of the Thesis is provided in this Chapter, with the most remarkable findings being summerized in order to highlight the strategies that have been derived to design novel functional components for efficient NIBs. After a brief introduction given in Chapter 1 on the scientific and technological context as well as the social and environmental impact of this research field, the outcomes of our studies are presented. In Chapter 2, the first-principles investigation on case-study anode materials is shown to be effective for the atomistic description of Na⁺ intercalation and migration mechanisms and the identification of key factors to promote these processes. TiO₂ anatase surfaces exhibit different capabilities toward Na⁺ uptake and storage, that we have unravelled through DFT+U calculations and CI-NEB method. The most favorable adsorption of Na⁺ at the (100) termination is ascribed to a convenient accommodation of the large cations on a surface step that maximizes the Na⁺-O²⁻ interactions and does not disturb much the crystalline lattice. However, the (001) surface is the most

active toward Na insertion in the subsurface, thanks to its peculiar structural features: the large surface lattice window allows for an easy diffusion of the large sodium cation. By including migration barrier calculations, we have provided a more reliable model compared to the mere adsorption of the Na ion on the surface. In this way, we could explain the experimental observation of high performances in NIBs with ${\rm TiO}_2$ NPs exposing the (001) surface termination. Our findings have also highlighted that the surface structural features directly determine the barrier heights: the size of the lattice window exposed by the surface inversely correlates with the migration energies, with the barrierless (001) displaying the largest accessible area for the intercalating sodium ion. We believe that the identification of this easy computable structural descriptor can be instrumental for the development of new nanostructured materials with a potential efficient Na uptake mechanism. The $2D-MoS_2/graphene$ system is presented as a thermodynamically stable heterostructure that can easily accommodate Na^+ within the interlayer spacing. The hybrid interface is characterized by a moderate graphene-to- MoS_2 charge transfer, leading to a metallic character in their band structures computed at the PBE-D3BJ level of theory. 1T- and 3R-phases mainly differ for their capability to host the Na ion and enable its diffusion. While 1T-MoS $_2$ exhibits more favorable Na^+ intercalation energies, migration seems to be easier in the 3R counterpart. Again, we have found that barrier heights along the MEP of Na migration derive from structural features: migration results to be hindered by short-range Na-S coordination. From these findings, we have suggested

defect engineering strategies to improve Na mobility, such as introduction of S vacancies. Structure-property relationship in the high-energy P2-type cathode, $Na_x Ni_{0.25} Mn_{0.68} O_2$ (NNMO), has been addressed and extensively discussed in Chapter 3. We have focused on the charge compensation mechanism occurring upon anionic redox activity. DFT+U-D3BJ calculations performed at different Na contents in NNMO have revealed that desodiation is coupled at first to $Ni^{2+} \rightarrow Ni^{3+}$ oxidation, and then up to Ni^{4+} and $\mathrm{O}^{2-}{\rightarrow}\mathrm{O}^{-},$ while Mn is electrochemically inert. Our results show that oxygen vacancies can easily form nearby the Mn-deficient site at low Na content (x = 0.125, *i.e.*, 4.5 V state of charge), preferably along Mn-O-Ni bonds rather than along Mn-O-Mn ones. The low-energy superoxidebased structures identified at x = 0.25 (*i.e.*, 4.0 V state of charge) act as possible intermediates along the oxide-to-oxygen evolution. At x = 0.125, molecular oxygen can be released from a Mn-deficient site with preferential breaking of Ni-O bond, while Fe substitution is shown to suppress the O_2 loss due to the increased TM-O covalency. Simple descriptors provided in our study, such as oxygen vacancy formation and TM-O₂ coordination energy, could be useful to set up the design of novel high-energy cathode materials with reversible capacity and high efficiency. Finally, we have reported our efforts for the development of safe and reliable electrolytes in Chapter 4. We first have focused on the simulation tools that could provide correct predictions of sodium transport into the Pyr₁₃FSI ionic liquid. By means of joint theoretical and experimental investigation, we have shown that polarizable force fields are required to this end, since we deal with large molecular ions interacting via non-covalent forces. Direct comparison of calculated and measured diffusion coefficients as function of concentration has revealed that sodium diffusivity effectively decreases with increasing viscosity (salt content), thus confirming a Walden-like behavior for this RT-IL/salt binary system. Still, we have analyzed the solvation layers in terms of spatial distribution function and outlined that formation of tight Na-FSI ion pairs at high concentration can inhibit sodium mobility through the electrolyte matrix. Optimization of electrolyte formulation seems to be crucial since the composition can directly affect the electrochemical properties. For this reason, we have also explored the performance of RT-IL/PEO-based electrolyte with different composition. The PEO Pyr* formulation has shown enhanced ionic conductivity and good cyclability with both HC- and NVPF-based electrodes in Na half cells at room temperature, thus emerging as a promising polymer electrolyte for NIB. As carefully described in Chapter 5, the use of state-of-the-art theoretical tools together with advanced experimental techniques has allowed to deliver new knowledge on several promising component materials and their structure-property relationships that are relevant for Na-ion battery applications.

The methodology described so far can be extended to similar systems that still exhibit room for improvement. On going studies are mainly focusing on some other classes of cathode materials, such as phosphate olivines (NaFePO₄) or NASICON-like systems (Na₃V₂(PO₄)₂F₃), to unveil structure and morphology-related properties that directly affect their electrochemical behavior. The in-depth investigation of transport properties at the electrode/electrolyte interface definitely represents the main challenge. To this end, multi-scale approach can enable the integration of differentsized systems and processes occurring on different timescales. We aim at exploring the most important interactions that are established at the TiO₂, $MoS_2/Graphene$ or NNMO surface boundary with PEO-based electrolytes and their effects on Na⁺ intercalation.

Upscaling the computational protocol can be highly beneficial for the overall understanding of the battery functioning. The cell performance is not necessarily the addition of single phenomena occurring in the individual components and many effects can be correlated. Optimization and development of full-cell configurations would also benefit from more complete and even realistic models. In this way, theory and experiments are intended to approach each other and attenuate their border. The mutual cooperation and the joint efforts have strong potential to become an unavoidable driving force to foster the innovation and production of highly performing NIB devices.

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