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Novel proton and metal-ion conducting polymers and block copolymers

Viviani, Marco

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Summary

The environmental and climate crisis we are facing calls for sustainable solutions. In addition to the application of circular economy principles, an energy transition towards renewable sources and electrification of transport and facilities is essential to reach “carbon neutrality” and limit annual global warming below 1.5 °C. Achieving such a substantial change in energy production, storage and usage, requires the revamping of known technologies, the discovery of new ones and the development of energy materials.

Polymers play a pivotal role in ensuring the necessary technological evolution of current and future technologies. In particular, ion- and electron-conducting polymers, enabled major technological breakthroughs in energy applications, especially in electrochemical devices ranging from organic photovoltaic cells to polymer electrolyte fuel cells. The development of high-performance electrochemical energy devices (EEDs) strongly relies on ion conducting polymers which find their main application as solid polymer electrolytes (SPEs). The use of SPEs drastically increases the performance, safety and sustainability of EEDs compared to liquid-based systems.

In this work, we focus on ion conducting polymers suitable for proton exchange membranes (PEMs) and lithium or magnesium SPEs. PEMs enable the development of polymer electrolyte membrane fuel cells, one of the most promising and efficient energy production devices. These are expected to play a crucial role in the energy transition towards renewable sources due to their flexibility, scalability, and *zero-emission* when hydrogen is used as fuel gas. On the other hand, lithium and magnesium secondary batteries have the capacity to cyclically store and release electrical energy, representing ideal EEDs to stabilize and compensate for the volatility of renewable energy production. The relevance of high-power density rechargeable lithium batteries is already visible in everyday life. However, electrification of the transport sector and transition towards renewable energy sources requires massive production of secondary batteries. This raises the issue of lithium scarcity. Accordingly, significant efforts are dedicated to the search for alternative metals, among which magnesium is very promising.

The synthesis of novel polymer electrolyte materials is tailored to the final application. However, in all cases, of paramount relevance are the influence of chemistry and nanomorphology over ion transport mechanisms. The interplay between chemistry, nanostructure and ion conductivity in solid ion conducting polymers has proven to be a key factor in the optimization of polymer electrolyte performance and represents the main topic of this PhD thesis.

In Chapter 1, an overview of the main aspects covered in this thesis is presented. Starting from the influence of morphology and chemistry over ion transport properties of proton exchange membranes (PEMs) and solid polymer electrolytes (SPEs). We then introduce the complexity in defining the nanostructures of these systems and correlations with their

specific transport properties, especially when multiple phases are present. The application of PEMs in fuel cells (PEMFC), spanning from low temperature (LT) to high temperature (HT) range applications, is discussed. The relevance of the block copolymer approach in controlling the nanomorphology and their extended use in the synthesis of sulfonated aromatic polymers (sAP) for intermediate temperature (IT) PEMFC is explained. Particular focus is dedicated to the class of sPSS and sPSO₂ polymers and block copolymers that inspired the work presented in chapters 2 and 3. After a focus on the state of the art on PEM for HT-PEMFC and the cross-linking strategies, a final section related to SPEs for lithium and magnesium-ion batteries aims to introduce the requisites for battery applications and the different aspects affecting ion conductivity in binary systems when charges are added from external sources (salts).

In Chapter 2, we describe a multiscale investigation of the drying processes spanning from film thickness variation to the nanomorphology evolution of a commercial solution of perfluorinated ionomer (Nafion™) and of a solution of synthesized sulfonated poly(phenylene sulfide sulfone) (sPSS). The differences in the chemical structures between Nafion™ and sPSS have a strong impact on the solution, gel and solid membrane behaviours of these polymers. Using an *in-situ* multi-technique approach, we monitored the membrane formation process at different times and spatial scales. X-ray scattering techniques at grazing incident angle (GISAXS/GIWAXS) were employed to follow the nanomorphology evolution over distinct drying stages. The sol-gel transition observed by X-rays was confirmed by electrochemical impedance spectroscopy (EIS) which revealed an abrupt increase in the samples' resistivity. The variation of the film thickness was monitored by UV-Visible light reflectance (LR) starting from the gel-film transition point where a well-defined film/air interphase parallel to the substrate is formed. In our study, we found that Nafion™ films evolve from a micellar solution through the formation of a phase-separated gel and form an oriented, well phase-separated supported membrane, confirming previous studies in the sub-micrometre range. On the other hand, sPSS films evolve from a complex electrolyte system formed by semi-rigid chains via the formation of a homogenous gel, showing phase separation only at the end of the drying process. The different chemical structure also affects the response of dry films to RH variations. The results obtained and the processing parameters adopted in our investigation provide useful insights regarding micron-scale membrane fabrication for fuel cell applications.

In Chapter 3, we propose a novel proton-conducting ABA triblock architecture by synthesizing a family of PS-*b*-sPSS-*b*-PS triblock copolymers with low disperse PS outer blocks ($\mathcal{D} < 1,2$). These low fluorine content polymers were produced via catalyst-free synthesis and “thiol-click” addition reactions. This strategy ensured good control over the composition and overcomes problems related to the presence of alien metal ions and high fluorine content. Aiming to explore the self-assembly of this system and its influence on ion conductivity, we synthesized a different PS-*b*-sPSS-*b*-PS with variable sPSS volume fraction f_{sPSS} values between $13\% < f_{sPSS} < 34\%$ and IEC between 0.3 and 1.3 meq g⁻¹. All BCPs were stable up to $T_d \approx 300$ °C and showed a high degree of phase separation. X-ray and TEM analysis provided evidence of three different nanostructures, namely, spherical, hexagonally

packed cylinders and lamellar. An estimation of the χ parameter defined a “*superstrong*” segregation regime ($\chi N \gg 100$) for all compositions, in good agreement with experimental observations. The block copolymer architecture provided dimensional stabilization against swelling at high relative humidity, thus limiting water uptake. The relevance of the nanomorphology and the IEC over transport properties was defined by proton conductivity measurements. While low IEC block copolymer with spherical morphology acted almost as an insulating material, a four-order magnitude “jump” in conductivity was observed for the cylindrical morphology. The highest conductivity (50 mS cm^{-1} @ RH95%, 90°C), however, was reported for the lamellar nanostructure also thanks to the highest IEC of all the synthesized block copolymers.

In Chapter 4, we propose a novel poly(phenylene sulfide benzimidazole) polymer (named PPSBi) with high sulfur content and side benzimidazole groups as potential material for HT-PEM. This molecular structure aims to combine the oxidative stability of sulfide linkages with the benefit of “grafting” bulky benzimidazoles in terms of solubility and doping rate. The pristine PPSBi suffered from poor filmability and brittleness. These issues were overcome by thermal epoxy-benzimidazole cross-linking with polyfunctional glycidyl polyhedral oligomeric silsesquioxane (g-POSS). The high free volume created by the bulky branched structure of g-POSS endowed fast acid uptake at mild conditions without severe loss of thermo-mechanical stability. All the membranes were thermally stable well above 160°C . Using a sufficient amount of g-POSS, membranes capable of reaching acid doping levels as high as 5.6 of PA per repeating unit were obtained without degradation of the thermal and mechanical properties. At high doping levels, encouraging proton conductivities ($>20 \text{ mS cm}^{-1}$) were measured in anhydrous conditions at 180°C . The incorporation of high sulfide content together with the cross-linking approach bestowed on the membranes exceptional oxidative stability. The radical scavenger behaviour of thioether linkages and the physical limitation to oxidant penetration, provided by g-POSS cross-linking, resulted in a remarkable synergic effect against oxidative degradation. Provided that a higher molecular weight of PPSBi is achieved to cope with the pristine poor filmability, the proposed synthetic strategy, combined with the use of g-POSS as cross-linker, represents an interesting approach to novel HT-PEM fabrication.

In Chapter 5, inspired by the promising results reported for SPEs based on poly(allyl glycidyl ether) (PAGE), we describe how we modified PAGE to include sulfur heteroatoms in their structures at different oxidation states. Starting from PAGE, poly(2-(ethylthio) propyl glycidyl ether) (PEthioPGE) and poly(2-(ethyl sulfone) propyl glycidyl ether) (PEsulfoPGE) were successfully synthesized via sequential “thiol-ene” click reaction and oxidation. Thus, fully amorphous polymers with T_g well below room temperature and thermal stability up to 300°C were obtained. The effect of the presence of and the oxidation state of the sulfur over the thermal and transport properties was investigated. An increase in oxidation state led to higher polarity of the side chain resulting in reduced segmental mobility and a 40°C higher T_g of PESulfoPGE (-37°C) compared to PAGE. All three synthesized polymers showed promising ion conducting properties when mixed with different lithium and magnesium salts. Generally, the polarity of the side chains in PEthioPGE and PESulfoPGE resulted in enhanced solvation properties toward lithium and magnesium chlorides compared to PAGE. However,

the observed chain stiffening affects the ion transport properties, especially in the case of LiTFSI and Mg(TFSI)₂. PAGE shows better ion transport when LiTFSI is used. In contrast, polymers containing functional polar side chains exhibit better ion conductivities than PAGE when LiCl is used. Extending the exploration of ion transport properties to magnesium salts, we found appreciable ion conductivities for complexes made with Mg(TFSI)₂ and MgCl₂. In some cases, such as when mixed with Mg(TFSI)₂, the reported ion conductivities outperform the benchmark PEO polymer at all temperatures reaching conductivities in the order of 10⁻⁴ S cm⁻¹ at 90°C. These aspects, together with the intrinsic absence of crystallization for both the neat polymers and the related Li and Mg complexes, constitute a great advantage for the future development of new polymeric materials for low and room temperature battery applications.