

Multiscale simulations of heterogeneous Li metal interfaces for next generation batteries

Arianna Massaro,¹Francesca Fasulo,²Aniello Langella,¹Ana B. Muñoz-García,²Michele Pavone¹

¹Department of Chemical Sciences, University of Naples Federico II, Via Cintia 21, 80126 Napoli, Italy

² Department of Physics “E. Pancini”, University of Naples Federico II, Via Cintia 21, 80126 Napoli, Italy

arianna.massaro@unina.it

Lithium Metal Batteries (LMBs) offer promising perspectives as next-generation energy storage technologies owing to great potentialities of Li metal anode featuring low electrochemical potential (-3.047 V vs. SHE), ultrahigh theoretical specific capacity (~ 3860 mA h g⁻¹), and low density (0.534 g cm⁻³) [1]. However, LMBs severely suffer from limited reversibility, inadequate long-term stability and safety issues, that are mainly associated to dendrites growth and formation of “dead lithium”. To boost the LMB development as a viable solution for efficient energy storage, engineering a solid-electrolyte interphase (SEI) able to mechanically resist to the lithium growth and thus forcing the formation of homogeneous lithium layers on the current collector can be key to mitigate the lithium chemistry and develop durable and effective anodes [2]. Tailored artificial SEIs are usually composed by a high variety of components with very different chemical nature, the heterogeneity being even more intricated at boundary with the metal surface. The intriguing yet challenging task of computational modelling relies in the need for accurate theoretical methods that are suitable to describe the different chemistries on a multiscale level with affordable computation costs. Developing such effective simulation tools is foreseen to provide atomistic insights into main mechanisms driving the SEI formation, so as to drive the rational design of stable and efficient LMBs. First, we address the vinylene carbonate (VC) reactivity on Li(001) surface [3]. As common additive to conventional electrolytes able to promote the formation of a stable and protective SEI, VC can undergo tangled decomposition and polymerization processes *via* reductive ring-opening reactions. By applying Density Functional Embedding Theory (DFET) combining hybrid DFT and semi-local GGA-based methods as feasible approaches to treat molecular VC derivatives with localized charge and Li metal, we show that the thermodynamically accessible mechanisms for the ring-opening reaction feature energy barriers in the range of 0.29-0.34 eV. Dissociation *via* cleavage at vinylic sites is more likely to occur and leads to a highly reactive intermediate that can undergo either further decomposition towards C₂H₂ and Li₂CO₃ formation or a polymerization process, in close agreement with experimental observations [4]. Then, we focus on structuring and dynamics of polyethylene oxide (PEO) on Li surface terminations. As good Li⁺ conductive polymer, PEO is envisaged for the production of highly performing electrolytes that could also meet sustainability and flexibility requirements for large-scale exploitations. Fine-tuning and control of PEO decomposition pathways is crucial to assess the early stages towards SEI formation at the PEO/Li interface. While recent evidence has reported the Li-induced breaking of PEO ether bonds toward the formation of lithium oxides domains and ethylene release [5], we aim at describing the reaction mechanisms with atomistic detail and investigate the effect of applied voltage, temperature and presence of salts.

References

- [1] J. Janek, *et al.*, *Nat. Energy*, 2016, 1, 16141
- [2] Z. Yu, *et al.*, *Cell Rep. Phys. Sci.*, 2020, 1, 7, 100119
- [3] F. Fasulo, *et al.*, *J. Mater. Chem. A*, 2023, 11, 5660
- [4] S. Grugeon, *et al.*, *J. Power Sources*, 2019, 427, 77
- [5] P. Liu, *et al.*, *Adv. Energy Sustainability Res.*, 2022, 3, 2100142

Acknowledgments

This work has been financed by the Research Fund for the Italian Electrical System under the Three-Year Research Plan 2022-2024 (DM MITE n. 337, 15.09.2022), in compliance with the Decree of April 16th, 2018”.