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Li-ion solvation shell in PVDF-Based Quasi-Solid Electrolytes: A Molecular Perspective Nicole Ceribelli1, Giovanni Di Liberto1 and Livia Giordano1 1Department of Materials Science, University of Milano – Bicocca, via R. Cozzi 55, 20125 Milano, Italy n.ceribelli@campus.unimib.it

The development of high-performance Lithium-metal batteries has long been at the forefront of energy technologies, with the electrolyte being often the limiting factor directly affecting the performance and safety of the battery [1,2]. Among solid electrolytes, poly-vinylidene difluoride (PVFD)-based electrolytes have attracted increasing attention due to their promising mechanical properties and wide electrochemical stability. However, despite the high polymer permittivity ($\varepsilon' \approx 10–11$) which should allow efficient salt dissociation, there is growing evidence that the ionic transport in (PVFD)-based electrolytes requires the presence of a non-negligible amount of a liquid solvent [3]. Recent experimental studies have argued that residual DMF solvent, which is used during the electrolytes preparation to dissolve the polymer-salt system, solvates Li+ and contributes to the ionic diffuson [4]. Understanding the Li+ solvation and diffusion mechanism across this quasi-solid electrolyte (QSE) and the role of residual solvent on these properties is critical to advance the development of these battery systems. The delicate balance of interactions between the different electrolyte components can be difficult to capture by classical force field. We then investigated in depth the role of DMF in the solvation and diffusion of Li+ via ab-initio computational methods [4,5,6]. First, the interaction of LiFSI salts with DMF molecules and PVDF chains has been computed by constructing Li+(FSI-)p(DMF)n(PVDF)m complexes. In addition, ab-initio molecular dynamics (AIMD) simulations have been performed to gain further insights on the diffusion of Li+(FSI-)p(DMF)n complexes in channels formed by PVDF chains. The atomic structures and binding energies (ΔE) of Li(FSI-)p(DMF)n(PVDF)m+ complexes, coupled with simulated Raman spectra, demonstrated that strong bonding occurs between Li+ ions and DMF molecules and that the amounts on the order of [DMF]/[Li+] ~ 2–3 are required to make QSEs able to practically work in a real environment [4]. Moreover, our AIMD simulations of extended LiFSI-DMF-PVDF system confirm the weak interaction between Li ion and PVDF and show the solvation structure of Li+, with DMF and FSI- ions solvating Li+ ions. Our results showed that the solvation shell is dynamic, and the diffusivity is higher in the presence of a DMF-dominated solvation shell, where the addition of the PVDF matrix can increase the diffusivity by providing structured diffusion channels, enabling better performance in agreement with the experimental results [4,6]. This molecular-level insight represent a step forward in understanding the diffusion mechanism of Li-ion in PVDF-based electrolytes and can be used for the rational design of next-generation electrolytes with improved performances. [1] K. Sashmitha, M. U. Rani, Polymer Bulletin 2023. [2] D. Zhou, D. Shanmukaraj, A. Tkacheva, M. Armand, G. Wang, Chem 2019. [3] Y. Wu, Y. Li, Y. Wang, Q. Liu, Q. Chen, M. Chen, Journal of Energy Chemistry 2022. [4] N. Vallana, E. Carena, N. Ceribelli et al. ACS Appl. Energy Mater. 2024. [5] E. Carena, L. Mezzomo, N. Vallana, N. Ceribelli et al. Small 2024. [6] N. Ceribelli, L. Giordano et al. submitted 2025.

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