Unveiling the Nature of Electrode/Electrolyte Interphases in Thin Film Batteries

Diyi Cheng, Ryosuke Shimizu, Jamie L. Weaver and Ying Shirley Meng

The past four decades have witnessed intensive research efforts on the chemistry, structure, and morphology of the solid electrolyte interphase (SEI) in Li-metal and Li-ion batteries (LIBs) using liquid or polymer electrolytes, since the SEI is considered to predominantly influence the performance, safety and cycle life of batteries. Compared with their liquid-electrolyte analogues, Solid State Electrolytes SSEs have drawn increased attention as they promote battery safety, exhibit a wide operational temperature window, and improve energy density by enabling Li metal as anode materials for next-generation lithium-ion batteries. Despite suitable mechanical properties to prevent Li dendrite penetration, relatively wide electrochemical stability windows, comparable ionic conductivities, and intrinsic safety, most SSEs are found to be thermodynamically unstable against Li metal, where SSE decomposition produces a complex interphase, analogous to the SEI formed in liquid electrolyte systems. As one of the most successful SSEs, LiPON has enabled an all-solid-state thin-film battery with a Li metal anode and a high-voltage $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) cathode to achieve a capacity retention of 90% over 10,000 cycles with a Coulombic efficiency over 99.98%,[1] indicating the presence of extremely stable interphases between LiPON and electrode materials. The superior electrochemical performance of LiPON against Li metal has attracted numerous research efforts aiming to understand the underlying nature of stable Li/LiPON interphase. Experimental efforts to identify this stable interphase of LiPON against Li metal, however, have been impeded by the limited characterization techniques available due to the low interaction volume of lithium, the amorphous nature of LiPON, and the extreme susceptibility of both lithium metal and LiPON to ambient air and probe damage[2,3]

Originating from the structural biology field, cryogenic focused ion beam (cryo-FIB) and cryogenic electron microscopy (cryo-EM) have recently been introduced to battery research, and have proven the ability to preserve and probe Li metal for quantitative structural and chemical analysis. Given the susceptibility of LiPON and Li under electron beam exposure, herein we combined cryo-FIB and cryo-EM to preserve the Li/LiPON interphase and characterize its chemistry and structure.[4,5] The observed structural and chemical evolution across the interphase identifies the SEI components to be Li_2O, Li_3N and Li_3PO_4, with a unique multilayer-mosaic distribution. According to these findings, we proposed a multilayer-mosaic SEI model. A combination of neutron depth profiling (NDP) and cryo-EM for elucidating the interfacial chemistry and structure between LNMO cathode and LiPON will also be covered, which offers valuable insights on LiPON's stability against high voltage cathode.

References

1. Li, J., Ma, C., Chi, M., Liang, C. & Dudney, N. J. Solid electrolyte: The key for high-voltage lithium batteries. Adv. Energy Mater. *5* (2015), 1–6.
2. Yu, X. A Stable Thin-Film Lithium Electrolyte: Lithium Phosphorus Oxynitride. J. Electrochem. Soc. *144* (1997), 524.
3. Wang, X., Zhang, M., Alvarado, J., Wang, S., Sina, M., Lu, B., Bouwer, J., Xu, W., Xiao, J., Zhang, J. G., *et al*. New Insights on the Structure of Electrochemically Deposited Lithium Metal and Its Solid Electrolyte Interphases via Cryogenic TEM. Nano Lett. *17* (2017), 7606–7612.
4. Cheng, D., Wynn, T. A., Wang, X., Wang, S., Zhang, M., Shimizu, R., Bai, S., Nguyen, H., Fang, C., Kim, M., *et al.* Unveiling the Stable Nature of the Solid Electrolyte Interphase between Lithium Metal and Lipon Via Cryogenic Electron Microscopy. Joule, *4* (2020), 11, 2484-2500

Biography

Dr. Y. Shirley Meng received her Ph.D. in Advance Materials for Micro & Nano Systems from the *Singapore-MIT Alliance* in 2005. Shirley currently holds the Zable Chair Professor in Energy Technologies and professor in Materials Science & NanoEngineering at University of California San Diego (UCSD). Dr. Meng is the principal investigator of the research group - Laboratory for Energy Storage and Conversion (LESC). She is the founding Director of Sustainable Power and Energy Center (SPEC) (2005-2020). In 2020, she is named as the inaugural director of Institute for Materials Discovery and Design (IMDD). Dr. Meng received several prestigious awards, including Michael Faraday Medal of Royal Chemical Society (2020), International Battery Association Battery IBA Research Award (2019), Blavatnik Awards for Young Scientists Finalist (2018&2019), IUMRS-Singapore Young Scientist Research Award (2017), C.W. Tobias Young Investigator Award of the Electrochemical Society (2016) and NSF CAREER Award (2011). Dr. Meng is an elected Fellow *of Electrochemical Society (FECS) and Fellow of Materials Research Society (FMRS)*. She is the author and co-author of more than 240 peer-reviewed journal articles, two book chapters and five issued patents. She is the Editor-in-Chief for *MRS Energy & Sustainability*. Shirley is the co-founder of Unigrid LLC.
Research Website: LESC http://smeng.ucsd.edu/