doi:10.1017/S1431927621004694
Microsc. Microanal. 27 (Suppl 1), 2021
© Microscopy Society of America 2021

Sweeping Potential Regulated Structural and Chemical Evolution of Solid-Electrolyte Interphase on Cu and Li as Revealed by Cryogenic Transmission Electron Microscopy

Yaobin Xu, Haiping Wu, Hao Jia, Ji-Guang Zhang, Wu Xu and Chongmin Wang

Pacific Northwest National Laboratory, Richland, Washington, United States

Lithium (Li) metal is one of the most attractive anode materials for rechargeable batteries due to its low electrochemical potential (-3.040 V vs standard hydrogen electrode), ultrahigh theoretical specific capacity (3860 mAh g^{-1}), and low density (0.534 g cm^{-3}) compared with other present anode materials (1). However, before the Li anode can become a viable technology, formidable challenges need to be overcome. One of the main obstacles restraining the improvement of Li based battery performance is the electrode/electrolyte interphase, which is the key to understand battery electrochemistry, as it is where the electron and Li^+ ion combine and then get stored in the Li metal (2). However, the structural and chemical evolution of this solid-electrolyte interphase (SEI) with respect to electrochemical operating condition remains barely established. Besides, the reactivity and sensitivity of SEI make it difficult to elucidate the nanostructure and chemistry of SEI. To overcome this challenge, the cryogenic transmission electron microscopy (cryo-TEM) technique widely used in structural biology has been used in battery studies recently, which could not only provide resolution to the sub-angstrom level but also give very high spatial resolution in chemical analysis simultaneously (3, 4).

Herein, we develop a unique method for imaging the evolution of SEI formed on the copper (Cu) foil under sweeping electrochemical potential as shown in Figure 1. Then we combine cryo-TEM (high spatial resolution) and energy-dispersive X-ray spectroscopy (EDS) (high chemical sensitivity) techniques to characterize the detailed structure and chemical evolutions of electrochemically formed SEI layers in the vinylene carbonate (VC)-free and VC-containing electrolytes, to establish the correlation between the electrochemical potential and the VC additive induced SEI structural and chemical variations (5). TEM observations were performed on 300 kV FEI Titan monochromated (scanning) TEM equipped with a probe aberration corrector under low dose condition.

As representatively shown in Figure 2, we find that the SEI formed in the electrolyte of $LiPF_6$/EC-EMC without VC additive is monolithic amorphous layer at the cut-off voltage of 1.0 V, and it changes to amorphous layer embedded with Li_2O particles at 0 V (Figure 2a-c). The SEI formed in the VC-containing electrolyte maintains amorphous layer embedded with Li_2O particles from 1.0 V to 0 V (Figure 2d-f). The SEI formed in VC-free electrolyte is thinner than that in VC-containing electrolyte at 1.0 V and then increases rapidly as the voltage decreases. In addition, the SEIs formed on the surfaces of Cu foil and Li metal are different in composition as shown in Figure 2g and 2h. The content of F continuously decreases from 10.9% (0 V) to 1.8% (below 0 V) in the VC-containing electrolyte, while the content of O increases from 32.1% (0 V) to 51.3% (below 0 V) and the content of F decreases from 41.3% (0 V) to 20.0% (below 0 V) in the VC-free electrolyte. The structure transformation and composition difference imply that further chemical reactions occur between Li metal, electrolyte and SEI formed above 0 V when the voltage is reduced to a negative overpotential. We believe these may also provide insight into the optimization of the electrode/electrolyte interphase and will be helpful in designing next-generation advanced rechargeable batteries.

https://doi.org/10.1017/S1431927621004694 Published online by Cambridge University Press

Acknowledgements

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under Contract DE-AC05-76RL01830 under the Advanced Battery Materials Research (BMR) Program and the US-Germany Cooperation on Energy Storage. The characterization work was conducted in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory (PNNL). PNNL is operated by Battelle for the Department of Energy under Contract DE-AC05-76RL01830.

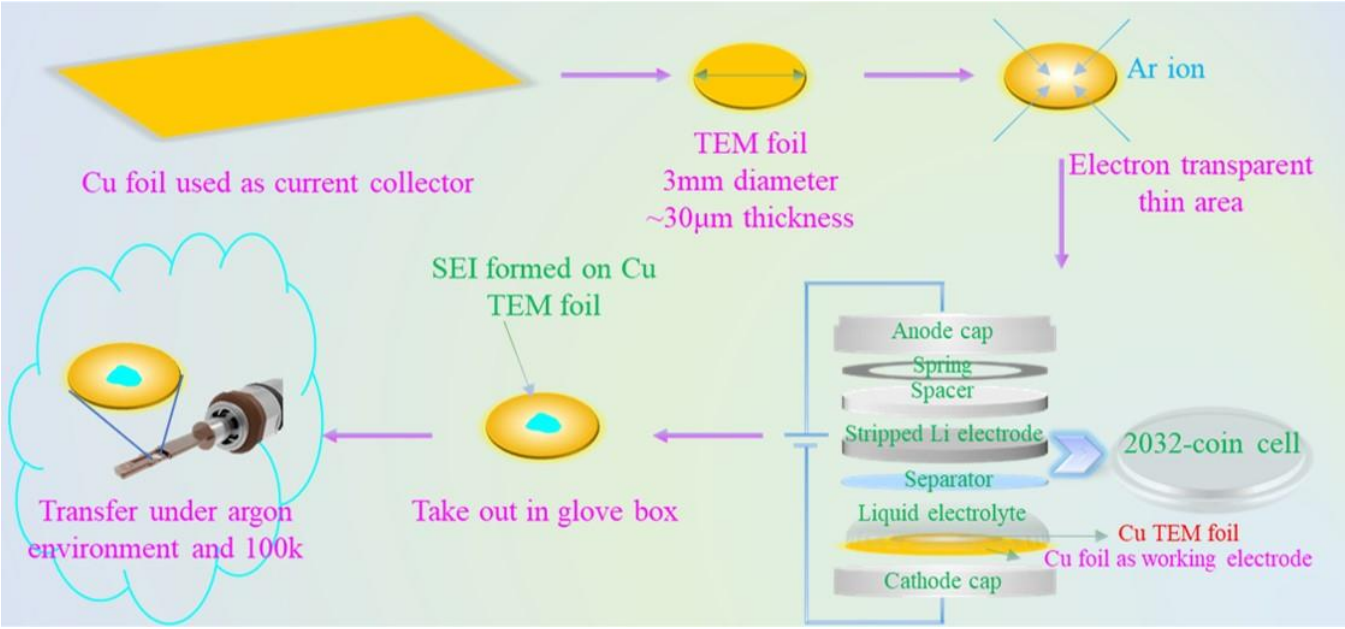

Figure 1. Figure 1. Schematic of preserving and stabilizing SEI formatted on Cu current collector by cryo-TEM. (a) Cu foil as current collector. (b) Cu foil with 3mm diameter prepared from Cu foil. (c) TEM foil prepared by precision ion polishing system. (d) Assemble TEM foil into coin cell. (e) Disassemble coin cell in glove box. (f) The TEM foil with SEI formed on is sealed in argon environment, plunged into liquid nitrogen and then transferred to cryo-TEM holder.

https://doi.org/10.1017/S1431927621004694 Published online by Cambridge University Press

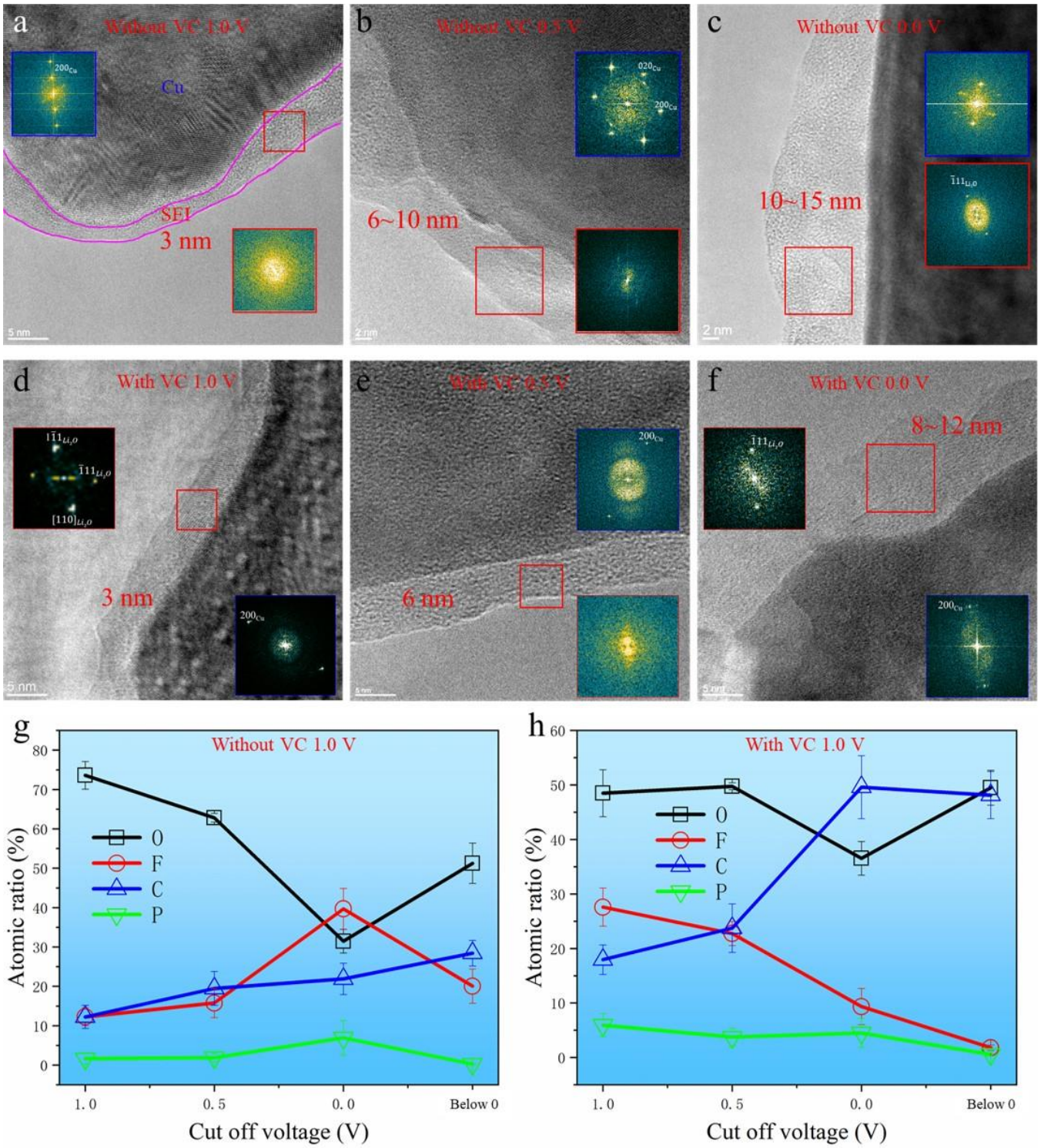

Figure 2. Figure 2. High-resolution TEM micrographs of SEI formed on TEM Cu foil in the electrolytes without/with 5% VC additive. (a-c) High-magnification images of the SEI formed on TEM Cu foil at different cut-off voltages of 1.0 V, 0.5 V and 0 V in the electrolyte without VC additive. (d-f) High-magnification images of the SEI formed on TEM Cu foil at different cut-off voltages of 1.0 V, 0.5 V and 0 V in the electrolyte with VC additive. Insets: FFT patterns from SEI (red) and Cu foil (blue). Atomic ratio of different chemical elements in SEIs formed on Cu and Li at different cut-off voltages of 1.0 V,

https://doi.org/10.1017/S1431927621004694 Published online by Cambridge University Press

0.5 V, 0 V, and below 0 V in the electrolytes (g) without VC additive and (h) with VC additive derived from EDS mapping.

References

[1] W. Xu, *et al*, Energy Environ. Sci. **7** (2014), p. 513.

[2] K. Xu, Chem. Rev. **114** (2014), p. 11503.

[3] Y.Z. Li, *et al*, Science. **358** (2017), p. 506.
[4] M.J. Zachman, *et al*, Nature. **560** (2018), p. 345
[5] Y.B. Xu, *et al*, Nano Energy. **76** (2020), p. 105040.

https://doi.org/10.1017/S1431927621004694 Published online by Cambridge University Press