

An Effective In-situ DRIFTS Analysis of the Solid Electrolyte Interface in Lithium Ion Battery

Atetegeb Meazah Haregewoin¹, Tzung-Da Shie¹, Shawn D. Lin^{1*}, Bing-Joe Hwang¹, Fu-Ming Wang²

¹Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan,

²Graduate Institute of Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan,

(*) sdlin@mail.ntust.edu.tw

Understanding the formation process, the composition and structure of the solid electrolyte interface (SEI) is important to elucidate how SEI may affect the performance of the lithium battery. Amidst the various techniques, FT-IR, which is non-destructive and surface sensitive, is a very powerful tool to differentiate functional groups based on their dipole moment. The use of ex situ FT-IR measurement leads to the interference of secondary reactions between the SEI layer and atmospheric contaminants such as H₂O, O₂, and CO₂ (1) which may obscure the real composition of SEI. In contrary to this, in-situ technique helps to circumvent these obstacles and not only to analyze materials under inert atmosphere but also at working electrode potential. Despite its excellent application as in-situ technique, in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is not widely used in the field of lithium ion battery. DRIFTS is more sensitive to surface species than transmission measurements. Unlike attenuated total reflectance (ATR), DRIFTS needs no conductor internal reflection element (IRE) and highly reflective surfaces (2). However, the design of the spectroelectrochemical DRIFTS cell is the core issue in this in-situ technique. In this work, we illustrated that our design of spectroelectrochemical cell worked effectively for in-situ DRIFTS analysis of the SEI layer in lithium ion battery.

The strong IR absorption of solvents is one of the key factors that were considered in designing in-situ spectroelectrochemical cell. Maintaining a thin layer of electrolyte between the working electrode and the IR window is crucial in minimizing the solvent masking effect (3). Fig. 1 shows schematic view of our in-situ FT-IR cell design with respect to the five mirrors in the spectrometer. The cell has a means of adjusting the working electrode against the window material to attain a thin layer of electrolyte. To maintain a constant concentration and to refresh the surface of the electrode, we developed a system to circulate the solution throughout the experiment. To make the cell leak tight, a chemically resistant epoxy (Torr seal) and Chemraz O-ring were used. The high solution resistance and asymmetric current distribution, which could arise due to the thin layer configuration, were reduced by employing a counter electrode with circular geometry which is situated behind the working electrode. All the materials used to construct the cell are chemically resistant.

The in-situ spectroelectrochemical measurement is illustrated with 1 M LiPF₆/EC+DEC (1:1) on MCMB working electrode. Platinum wire was used as a counter electrode and lithium foil as reference electrode. The cell was assembled and the electrolyte preparation was done inside the glove box. The electrolyte was kept in a separate container until we took the background spectrum from the bare electrode. Thereafter, the cell is filled with electrolyte with the aid of pump and circulated throughout the experiment. FT-IR spectrum was recorded at open

circuit potential (OCV) using bare electrode spectrum as a background after maintaining the cell for 2h at OCV of about 3.0 V_{Li/Li+}. Then, FT-IR spectra were recorded using the bare electrode as a reference spectrum after the potential was linearly scanned down in the negative direction to 2.5, 1.8, 1.2, 0.8, 0.6, 0.4, and 0.2 V within 5 min holding period at each potential.

The OCV spectrum was resolved to contain mainly the electrolyte contribution. To eliminate the thin layer electrolyte contribution at each potential, we subtracted the OCV spectrum from each potential spectrum (Fig. 2). The result shows the presence of different film formation steps in the process. The first formation is observed in the region between 1.8 to 1.2 V which is due to the reduction of trace amount of water and its subsequent reaction with the electrolyte. Film formation due to reduction of the electrolyte and its subsequent interactions is observed in the region between 1.2 to 0.8 V and below 0.8 V. The FT-IR spectra obtained after subtraction between two successive potentials also supports this observation. Details of reduction mechanism can be proposed accordingly using the fundamental chemical reaction mechanistic steps and theoretical DFT calculation when needed.

Our approach illustrated in this work has a good consistency with the reduction mechanism proposed in the literature. This technique will help shed light in to our understanding of the formation and the composition of SEI.

We are grateful to Ministry of Economic Affairs of Taiwan, ROC (101 EC-17-A-08-S1-183) for the financial support.

References

1. S. Amalraj, D. Aurbach, Journal of Solid State Electrochemistry, 15 (2011) 877-890.
2. P. R. Griffiths, J. A. de Haseth, Fourier Transform Infrared Spectrometry, 2nd ed., John Wiley & Sons, Inc. 2007, 349-362
3. P. Christensen, A. Hamnett, Electrochimica Acta 45 (2000) 2443-2459

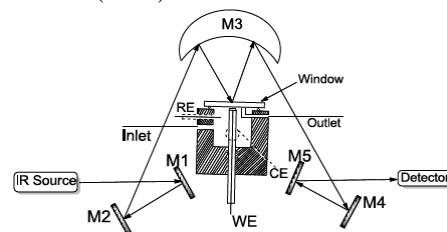


Fig. 1 Schematic view of in-situ FT-IR cell with respect to the five mirrors in the spectrometer.

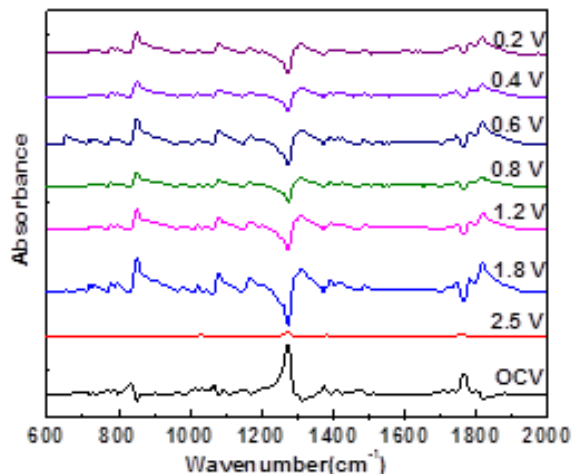


Fig 2. In-situ DRIFT spectra of 1 M LiPF₆/EC+DEC (1:1) at different potential after subtracting the OCV from each spectrum.