Controlling the coordination states of electrolyte solutions for reversible lithium metal plating/stripping

Tomohiro Obukata [a], Yuki Yamada [a], Atsuo Yamada [a]
[a] The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

E-mail: obukata@btr.t.u-tokyo.ac.jp

Lithium metal is an ideal negative electrode for its high theoretical capacity. However, the dendritic growth and poor coulombic efficiency have prevented its practical application to a rechargeable battery. Of particular importance is the development of stable and functional electrolyte solutions. A promising candidate is highly concentrated electrolytes, which show an unusual passivation ability owing to its unique coordination state.[1] Recently, highly concentrated ether-based electrolyte is reported to effectively address those issues of lithium metal negative electrodes, implying a coordination state is an important factor that dominates the reversibility of electro-deposition/dissolution of lithium metal. In this study, we investigated the coordination state of ether-based electrolytes, and discuss its effect on the reversibility of lithium metal negative electrodes.

We first studied lithium metal deposition/dissolution in $LiN(SO_2F)_2$ (LiFSI) / tetrahydrofuran (THF) electrolytes at various concentrations (Fig. 1a). We found that a concentrated 4.0 M LiFSI/THF electrolyte showed higher coulombic efficiency. As a key difference of the electrolyte solutions, we found extensive coordination of Li^+ to FSI anion in the concentrated electrolyte (Fig. 1b). We next diluted the highly concentrated LiFSI/THF electrolyte with non-polar toluene, motivated by previous works on diluted solvate ionic liquids[3], which have higher ionic conductivity and lower viscosity, still showing a local coordination structure similar to original solvate ionic liquids. The LiFSI/THF:toluene electrolyte showed comparable or even better coulombic efficiency than the concentrated LiFSI/THF electrolyte (Fig. 1a). The Raman spectrum shows a similar coordination environment achieved with the addition of toluene (Fig. 1b), suggesting a correlation between the coordination states of electrolyte solutions and the reversibility of lithium metal negative electrodes. This work shows that the high reductive stability unique to highly concentrated electrolytes is also available in diluted ones.

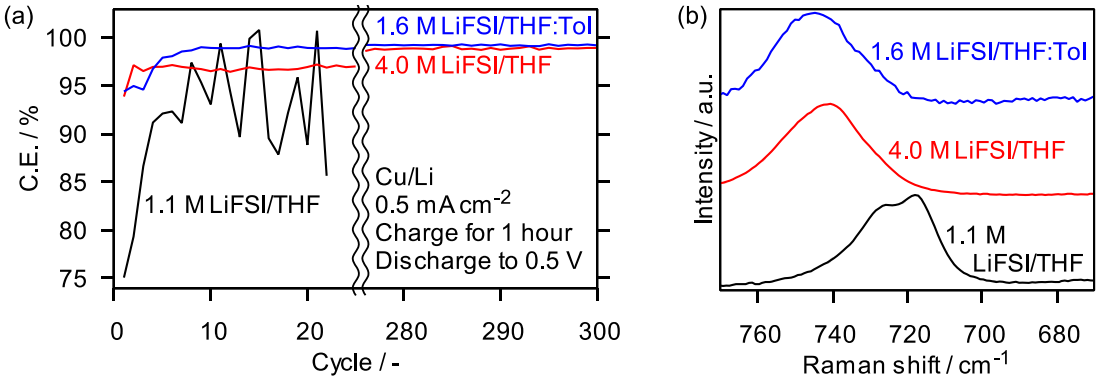

Fig. 1 (a) Coulombic efficiency and (b) Raman shift of the counter anion with each electrolyte.

References:
[1] Y. Yamada, K. Furukawa, K. Sodeyama, K. Kikuchi, M. Yaegashi, Y. Tateyama, A. Yamada, J. Am. Chem. Soc., 2014, 136, 5039.
[2] J. Qian, W. A. Henderson, W. Xu, P. Bhattacharya, M. Engelhard, O. Borodin, J.-G. Zhang, Nat. Comm., 2015, 6, 6362.
[3] K. Ueno, J. Murai, H. Moon, K. Dokko, M. Watanabe, J. Electrochem. Soc., 2016, 164, A6088.