Supporting Information

In Situ Observation of Electrolyte-Concentration-Dependent Solid Electrolyte Interphase on Graphite in Dimethyl Sulfoxide

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Electrochemical Characterization

The electrochemical behavior of natural graphite electrodes in the as-prepared LiTFSI/DMSO electrolytes at various salt concentrations is characterized by galvanostatic cycling. Figure S1a compares the potential curves of natural graphite in 1.0, 2.65, and 3.37 mol dm$^{-3}$ LiTFSI/DMSO electrolytes. In 1.0 mol dm$^{-3}$ LiTFSI/DMSO electrolyte, the electrode potential gradually decreases from 1.5 V to 1.1 V. A potential plateau at 1.1 V is observed. It has been demonstrated that the capacity at the potentials over 1.0 V is attributed to the co-intercalation of DMSO with lithium ion into graphite. A wide potential plateau at the potential of 0.9 V could be attributed to continuous decomposition of intercalated electrolyte accompanied by the deterioration of graphite layers.\(^1\)

The behavior of natural graphite in 3.37 mol dm$^{-3}$ and 2.65 mol dm$^{-3}$ LiTFSI/DMSO electrolytes are completely different from that in the dilute solution. The absence of plateau over 0.9 V indicates that the co-intercalation of solvent is significantly suppressed. A plateau is observed at potentials of 0.2–0.01 V. This capacity is attributed to the intercalation of lithium ion into graphite.\(^2\) Thus, it is obvious that the behavior of graphite significantly depends on the salt concentration of LiTFSI/DMSO solutions. In addition, it is found that there exists obvious different initial capacity in the two concentrated electrolytes. Figure S1b,c displays the first three discharge-charge profiles of graphite in 3.37 and 2.65 mol dm$^{-3}$ LiTFSI/DMSO electrolytes, respectively. In 3.37 mol dm$^{-3}$ LiTFSI/DMSO electrolyte, the reversible capacity increases with cycling. The increase of capacity is presumably due to
activation of more material to react with electrolyte during cycling. However, there is no such an activation process observed in 2.65 mol dm$^{-3}$ LiTFSI/DMSO electrolyte. The highly concentrated electrolyte is of high viscosity, hence it is difficult for 3.37 mol dm$^{-3}$ LiTFSI/DMSO electrolyte to well infiltrate the electrode. According to galvanostatic cycling experiments, we find that the discharge-charge performance of graphite electrode in 3.37 mol dm$^{-3}$ LiTFSI/DMSO electrolyte could be significantly increased when the current density is reduced from 0.1 C to 0.05 C.

Figure S1d compares the cycling performance of graphite electrodes in the two concentrated electrolytes. In 3.37 mol dm$^{-3}$ LiTFSI/DMSO electrolyte, the charge capacity retains 300 mA h g$^{-1}$ after 50 cycles. In 2.65 mol dm$^{-3}$ LiTFSI/DMSO electrolyte, the charge capacity is slightly higher than that in 3.37 mol dm$^{-3}$ LiTFSI/DMSO electrolyte until the 40th cycle. After 50 cycles, the capacity deteriorates to 260 mA h g$^{-1}$. 
**Figure S1.** (a) Potential curves of natural graphite electrode in 1.0 mol dm$^{-3}$, 2.65 mol dm$^{-3}$, and 3.37 mol dm$^{-3}$ LiTFSI/DMSO electrolytes. Discharge-charge curves of natural graphite electrodes in 3.37 mol dm$^{-3}$ LiTFSI/DMSO electrolyte (b) and 2.65 mol dm$^{-3}$ LiTFSI/DMSO electrolyte (c). (d) Cycling performance of natural graphite electrode in 3.37 mol dm$^{-3}$ and 2.65 mol dm$^{-3}$ LiTFSI/DMSO electrolytes.

**In Situ AFM of HOPG Electrode in 2.65 mol dm$^{-3}$ LiTFSI/DMSO Electrolyte**
Figure S2. (a-f) 3D AFM images of HOPG electrode in 2.65 mol dm\(^{-3}\) LiTFSI/DMSO electrolyte during the first cycle (correspond to Figure 4). The scan area is 2×2 μm.

Figure S3. In situ AFM images of HOPG electrode in 2.65 mol dm\(^{-3}\) LiTFSI/DMSO electrolyte after the first cycle (a) and after the second cycle (c). (b) 3D AFM image corresponds to image (a). (d) 3D AFM image corresponds to image (c).

REFERENCES
