

Tuning the solid electrolyte interfacial layer of lithium metal anode with fluoroethylene carbonate-based electrolytes toward high cycling stability of Li metal batteries

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Rechargeable lithium metal batteries have received a great attention due to their high potential in achieving high energy density, which is based on the low redox potential (-3.04 V vs SHE) and high theoretical capacity (3860 mAh g⁻¹) of Li metal.^[1] However it has big challenges due to uneven Li ion stripping/plating on Li metal electrode and Li metal corrosion by the electrolyte during repeated battery cycling process. For inducing uniform Li deposition and stripping and preventing the electrolyte deposition, formation of stable solid electrolyte interface (SEI) is important. A strategy for forming a stable and robust SEI is adding some additive such as fluoroethylene (FEC)^[2], vinylcarbonate^[3], LiNO₃^[4] and polysulfides.^[5] Among these additives, the FEC is well known to be effective additive in stabilizing lithium metal due to LiF which has ionic conductivity of 10⁻⁶ S cm⁻¹^[6], and the polycarbonate which imparts a flexibility to SEI layer.^[7]

In this work, the FEC-containing electrolytes were intensively investigated for the use in lithium metal batteries, and the efficacy of the FEC based-electrolytes was confirmed. The stabilization of Li metal electrode was clearly observed for 1M LiPF₆ EC/DEC (5/5) with 10 wt% FEC and 1M LiPF₆ FEC/DEC (3/7) electrolyte. However, for the FEC content of 50 vol% and above, the discharge capacity and cycling stability of Li/LCO cell were reduced due to the formation of resistive layer on cathode, indicating the existence of an optimum FEC content for a practical use. In terms of ionic conductivity and Li metal cycling stability, the FEC/DEC electrolyte volume ratio of 30/70 was a promising candidate for high performance Li metal batteries. The Li/LCO cell with 30FEC/70DEC electrolyte showed a capacity retention of 97.5 % and coulombic efficiency of 99% even after 300 cycle. From 3-electrode impedance analysis, the anode impedance of control sample (EC/DEC) was dramatically increased during cycling process due to production of resistive porous layer. However, the anode impedance from 30FEC/70DEC electrolyte showed The XPS analysis clearly showed that LiF and polycarbonates are formed in the FEC-derived SEI layers. The diameters of rod-like Li deposits for the FEC/DEC electrolytes were order of magnitude larger than that of the EC/DEC electrolyte. The results imply that the SEI layer with high Li ion conductivity and high elastic property can allow lateral growth of Li deposits and accommodate the resulting volume expansion of the Li deposits.

References:

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