Manganese Trapping by Polymeric Macrocycles in Li-Ion Batteries: What Works, What Doesn't, and Why.

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A well-known major degradation mechanism for Li-ion batteries performance is initiated by the dissolution of transition metal cations from the positive electrode. These cations will migrate to and deposit on the negative electrode surface, and subsequently cause the catalytic reduction of solvent molecules with attendant excessive surface film (SEI) growth. This process consumes electrochemically active Li and degrades the battery performance (manifested by capacity fading and increased cell resistance). A common approach to preventing this degradation is the deposition of nanometer–scale inorganic barrier films (such as Al_2O_3 or AlF_3) on the positive or the negative electrode. Another proposed solution for this problem is the reduction of the SOC swing during cell operation. Both known mitigation measures have drawbacks and neither is 100% effective. We propose an alternative (and complementary) measure: trapping of dissolved Mn^{+2} cations by tethered macrocycles placed in the inter-electrode space, to prevent their deposition at the negative electrode. We will present high temperature (50°C) galvanostatic cycling data for $LiMn_2O_4$-graphite cells and discuss the Mn^{+2} trapping behavior of in-house synthesized 15-crown-5, 18-crown-6 ethers and their aza-substituted versions, when tethered to various polymers. Data from several analytical techniques (^{13}C MAS-NMR, SEM, elemental mapping by X-ray fluorescence, XPS, XANES and XAFS) are used to elucidate the observed behavior and explain why some materials trap Mn and improve the high temperature capacity retention in $LiMn_2O_4$ graphite cells, while others don't.