High voltage LIB cathodes enabled by salt-reinforced liquid electrolytes

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Abstract

We report on electrochemical properties of $\text{Li/Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ secondary batteries in electrolytes designed to stabilize electrodeposition of lithium. Ethylene carbonate (EC): dimethyl carbonate (DMC) containing a LiPF_6/LiF salt blend stabilizes lithium electrodeposition and enables $\text{Li/Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ batteries with a high discharge capacity of 270mAh g^{-1} at 0.05mA cm^{-2} . Cells containing the LiF -reinforced electrolytes also exhibit excellent capacity retention over 500 cycles with Coulombic efficiencies approaching 100%. Post-mortem SEM analysis of the lithium anode shows more compact deposition in the presence of the LiF salt additive, while XPS depth profile analysis of cathodes show a more uniform distribution of Mn over the first 180 nm from the electrode/electrolyte interface. The results imply that LiF reinforced electrolytes simultaneously facilitate stable lithium electrodeposition and reduce Mn dissolution.

Key words: lithium-ion battery; high voltage cathode; lithium fluoride

Introduction

Research into high voltage and high capacity electrode materials has received intensive interest in recent years because of the improvements in energy density these cells offer in the well studied lithium ion battery platform. Rechargeable LIBs employing cathode materials with high operating voltage (e.g. 5V vs. Li/Li^+) and high specific capacity ($> 250\text{mAh g}^{-1}$) are among the most sought after cell configurations for enabling high-energy storage technologies for applications in portable devices, transportation, and advanced robotics [1-3]. Cathodes based on transition metal oxides containing Mn, Ni, Co, or Mn-based spinels have been researched extensively. Lithium-rich layered oxides (e.g. $\text{Li}_{1.2}\text{Mn}_{0.525}\text{Ni}_{0.175}\text{Co}_{0.1}\text{O}_2$ [4]) and two-electron materials (e.g. $\text{Li}_2\text{Mn}_x\text{Fe}_{1-x}\text{SiO}_4$ [5]) containing electrochemically active Mn are among the most promising because of their high specific capacity upon charging over 4.5V vs. Li/Li^+ . Mn-containing cathode materials such as $\text{LiCrMn}_2\text{-yO}_4$ [6] and $\text{Li}_2\text{FeMn}_3\text{O}_8$ [7], have also been proposed. To access the high storage capacity of these cathodes, the electrode must be fully activated and the electrolyte must be stable at high voltages during the initial charging process. Conventional electrolytes used for LIBs (e.g. EC:DEC, EC:DMC in LiPF_6) will decompose continuously above 4.5V vs. Li/Li^+ , leading to high interfacial impedance and capacity fading [1,8-9].

To accommodate the demand of high voltage and capacity cathode materials, many studies have explored functional electrolytes, such as ionic liquids, polymers, and aprotic liquids containing protective additives [10-12], which offer high oxidation voltage. Challenges associated with the high viscosity, low ionic conductivity, poor round-trip efficiency, and high Mn loss upon extended cycling continues to present significant barriers to adoption of these electrolytes. Of the various electrolyte solvent options organic carbonates are still considered among the most promising because of their high dielectric constant, low viscosity, low activation energy for lithium ion diffusion and excellent ability to dissolve lithium salts.

Recently, we reported that propylene carbonate-based liquid electrolytes reinforced with LiF facilitate fast lithium diffusion at the electrolyte-electrode interface, and thereby stabilize lithium electrodeposition [13]. It was shown that in $\text{Li/Li}_4\text{Ti}_5\text{O}_{12}$ (Li/LTO) half-cells containing thin and thick LTO electrodes that these

electrolytes enable long-term stable cycling with a capacity enhancement of around 40% [13]. Previously, Shiraishi et al [14] reported that carbonate-based electrolytes containing HF generate a stable SEI layer on lithium metal and promote smooth lithium deposition. Zhang et al [15] reported that electrolytes based on fluorinated cyclic or linear carbonates accommodate a 5V $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode due to their high oxidation potential and superior anodic stability. The high toxicity of HF and slow dissolution of Mn in fluorinated carbonates present unresolved challenges for adoption of either of these strategies for designing practical batteries. We herein report on electrochemical performance of $\text{LiF}+\text{LiPF}_6/\text{EC}:\text{DMC}$ electrolyte in Li/Li-rich NMC [16]. We find that LiF dissolved in the electrolyte facilitates stable electrodeposition of lithium in symmetric cells and reduces dissolution of Mn from the cathode. Additionally, we find that Li/ $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ half-cell employing $\text{LiF}+\text{LiPF}_6/\text{EC}:\text{DMC}$ electrolytes exhibit improved capacity retention and cycling performance over at least 500 cycles. These results underscore the importance of LiF as a SEI additive in rechargeable LIBs [17].

Experimental

EC, DMC and LiPF_6 (Aldrich) were dried using our previously reported method [18] and kept under Argon. Electrolytes with y M LiPF_6 + (1-y) M LiF in EC:DMC (v:v=1:1) were prepared in a glovebox and kept on 3Å sieves for at least one week before use. $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ (NMC) electrodes were provided by the U.S. Department of Energy's (DOE) Cell Fabrication Facility, Argonne National Laboratory. [The active material comprises 92% of the mass of the Li-rich NMC electrode.](#)

Symmetric lithium coin cells and Li/ $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ half-cells (type 2032) were assembled in an Ar-filled glovebox. O-ring PTFE and glass-fiber separators were used for symmetric cell and half-cell studies, respectively. A Neware CT-3008 tester was used for cycling tests. [The voltage cut-off for electrolytes without LiF is 2-4.6V and 2-4.9V for electrolytes containing LiF.](#) The Li-rich NMC was analyzed using scanning electron microscopy, energy dispersive X-ray analysis (SEM, LEO1550-FESEM) and X-ray Diffraction (Scintag Theta-Theta X-ray Diffractometer). The composition profile of Mn in the cathode was characterized by X-ray photoelectron spectroscopy (XPS) using a Surface Science Instruments SSX-100 with operating pressure around 1×10^{-8} Torr. Monochromatic AlK-alpha x rays (1486.6eV) were used with a beam diameter of 1mm and photoelectrons were collected at a 55-degree emission angle. A hemispherical analyzer determined the electron kinetic energy, using a pass energy of 150V for wide/survey scans, and 50V for high resolution scans. Samples were etched using 4kV Argon ions over a 2x4 mm area with 5 microamp beam current.

Results and discussion

The morphology of $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ was studied using SEM and elemental mapping. SEM analysis shows that the powder contains aggregates of spherical particles with diameters between 60 and 80nm. Ni, Mn, and Co maps of the particles from EDX are displayed in Fig. 1(e&f). It is apparent that the three elements are distributed throughout the carbon particles. The XRD pattern of NMC shown in Fig. 1(d) is consistent with previous reports [19].

Fig. 2(a) and (b) show the galvanostatic charge/discharge profiles obtained in Li| LiPF_6 in EC:DMC| $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ with/without LiF. The half-cells were aged for one month before cycling, allowing sufficient diffusion of the electrolyte into the preformed cathode. Both results are generally consistent with the characteristics profiles of Li-rich NMC in 1 M $\text{LiPF}_6/\text{EC}:\text{DMC}$ electrolytes [19]. Plateaus in the (3.5-4.7) V range are observed to shift to higher voltages with the increase of current density and cycle number. A plateau between 3.5-4.5V is associated with the oxidation of nickel and cobalt compounds while the region between 4.5-4.7V is related to the structure transformation of Li_2MnO_3 . Figure 2(b) shows that 30mol% LiF in the electrolyte delivers a capacity of 270 mAh g^{-1} in the first discharge cycle at 0.05 mA

cm^{-2} (C/24), which is about 70 mAh g^{-1} higher than for the control electrolyte, without LiF. The current density was gradually ramped up to 0.4 mA cm^{-2} (C/3) over 400 cycles and discharge capacities of 270, 247, 223 and 191 mAh g^{-1} at C/24, C/12, C/6, and C/3 rate, respectively, were obtained. It is noticed that without LiF in the electrolyte, the cells are hardly able to reach 4.9V. Fig. 2(c) and (d) show the capacity retention and columbic efficiency upon extended cycling, at 0.4 mA cm^{-2} (C/3), for Li|LiF+LiPF₆ in EC:DMC|NMC with different concentrations of LiF. Addition of as little as 5 mol% LiF produces substantial improvements in capacity retention after the 270th cycle, while addition of 30% LiF yields even larger improvements, with the cells able to retain a capacity of nearly 150 mAh g^{-1} after 500 cycles. In contrast, half-cells based on electrolytes without LiF fail catastrophically after around 270 cycles [4].

Voltage profiles measured in galvanostatic cycling of symmetric lithium cells in electrolytes with/without LiF are reported in Figures 3(a) and 3(b). Each half cycle lasts for 3 hours at 0.2 mA cm^{-2} and the total charge passed is 2.16 C cm^{-2} - enough to short-circuit the cell. [The electrolyte without LiF shows an erratic voltage response \(Fig. 3\(a\)\)](#). In contrast, Fig. 3(b) shows that cells containing 30% LiF cycle stably over 1920h (2.67months). Post-mortem SEM analysis of the Li anode (Fig. 3(c) & (d)) compares the surface morphology of the electrodes after 1920h cycling. Prior to these measurements the lithium electrodes were washed with a pure EC:DMC mixture. Cells without LiF form thick, loose dendritic structures while those containing LiF exhibit finer, more compact surface structures. To study the effect of LiF on the electrochemical stability of the electrolytes, an electrochemical floating test was performed on Li/Li-rich NMC cells in the potential range 4.7 to 5.5V. As shown in Fig. 3(e), electrolytes without LiF show an increase of current as the potential increases and exhibit, an unstable time-dependent current response when the potential is held at 5.5V. In contrast, electrolytes containing LiF exhibit much lower current response and display attractive stability at least up to 5.5V. It suggests that in addition to its beneficial effects on lithium electrodeposition, addition of LiF enhances the potential limit of the electrolytes in the high voltage range, which leads to the improved cycling performance. To study the effect of LiF on the cathode, Li-rich NMC cathodes harvested after 250 cycles (electrolytes containing no LiF) and after 500 cycles (30% LiF) were characterized using XPS measurements. Fig. 3(f) and (g) reports the intensity of photoelectrons with binding energies ranging from 637 to 646 eV, associated with Mn in the cathode, at depths from 0 to 180 nm from the electrode/electrolyte interface. It is apparent that for electrolytes containing LiF, the Mn spectra at the surface is essentially identical to that in the bulk electrode. For electrolytes without LiF, the Mn XPS spectra become progressively more attenuated as the interface is approached. [The results are supported by a larger number of measurements \(not shown\) employing electrodes before failure, which show no change in XPS intensity with distance from the electrode/electrolyte interface whether or not LiF is present in the electrolyte](#). These results are consistent with a greater loss of Mn from the electrode surface layer in electrolytes without LiF at the time of failure. The results in Fig. 3 therefore indicate that LiF salt additives can not only facilitate stable lithium electrodeposition, but may also enhance the lifetime of Li-rich NMC cathodes by limiting Mn dissolution in the electrolyte at high voltages.

Conclusion

In summary, we have investigated rechargeable batteries based on Li-rich NMC cathodes, Li metal anode, and a liquid electrolyte containing LiF. We find that batteries containing 30mol% LiF exhibit capacity enhancements as high as 35% and largely improved cycling stability over 500 cycles. LiF appears to improve performance by two processes: (i) it increases the high voltage stability of the electrolyte, and (ii) it reduces Mn dissolution at the cathode.

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Figure Captions

Fig. 1. Surface analyses of the Li-rich NMC cathode: SEM images at various magnifications (a-c), XRD pattern (d), EDX spectrum (e), and elemental mapping (f).

Fig. 2. Voltage vs. capacity profiles for the Initial, 10th, 50th, 100th, 250th/500th without LiF (a) and with 30% LiF (b). Discharge capacity retention (c) and coulombic efficiency (d) of Li/Li-rich NMC with 30mol% LiF+LiPF₆/EC:DMC, 5mol% LiF+LiPF₆/EC:DMC and LiPF₆/EC:DMC electrolytes at room temperature. The current density increases from C/24, C/12, C/6 to C/3.

Fig. 3. Electrode surface stability measurements in contact with LiPF₆/EC:DMC, 20mol% and 30mol% LiF+LiPF₆/EC:DMC electrolytes: (a)(b) galvanostatic cycling in symmetric lithium coin cells at 0.2 mA cm⁻²; (c)(d) post-mortem SEM images of lithium surface harvested after galvanostatic cycling; (e) Constant voltage-charge profile of Li/ Li-rich NMC cells maintained at 4.7V, 4.9V, 5.1V, 5.3V and 5.5V for 5 hours at room temperature; (f)(g) post-mortem XPS analyses of Mn in NMC electrodes after cycling tests.

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Figure 1

Figure 2

Figure 3