Evaluating the effect of solid electrolyte interphase formers on lithium depth profiles of the solid electrolyte interphase layer and bulk electrode material in $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$/graphite pouch cells obtained with lithium nuclear reaction analysis

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ABSTRACT

Lithium loss resulting from positive electrode deterioration and lithium accumulation within the solid electrolyte interphase (SEI) at the negative electrode leads to charge capacity loss in lithium-ion batteries (LIBs). We present a novel method to quantify origins of capacity loss resulting from positive electrode degradation and lithium immobilization within the SEI by comparative lithium depth profiles using Lithium Nuclear Reaction Analysis (Li-NRA). $Li(Ni_{0.4}Mn_{0.4}Co_{0.2})O_2$/artificial graphite (NMC442/AG) pouch cells were cycled with electrolytes containing 1 M $LiPF_6$ in either 1:1 ethylene carbonate (EC)/dimethyl carbonate (DMC) or DMC with 3% vinylene carbonate (VC) SEI former. Lithium accumulated rapidly within the SEI in cells containing EC as compared to cells containing VC. Lithium loss from the positive electrode occurred at a linear rate, after formation, which was independent of electrolyte composition tested. The technique and methods provide quantitative insight into the impact of materials on capacity loss.

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1. Introduction

Electric vehicles with greater range and durability will require lithium ion batteries (LIBs) with improved energy density and materials stability [1]. Utilization of high energy density materials in LIBs, such as nickel rich positive electrodes, has been impeded by rapid charge capacity loss observed in the novel systems [2–4]. Charge capacity loss in LIBs is frequently attributed to lithium-ions loosing reversible host sites in the positive electrode and immobilization of lithium-ions in the solid electrolyte interphase (SEI) at the negative electrode [5–8].

Positive electrode degradation in the popular nickel manganese cobalt (NMC) positive electrode material has been attributed to phase change, transitional metal dissolution and oxygen loss [9,10]. Recent work by Borger et al. and Vortmann-Westhoven et al. showed in commercial cells of different positive electrode chemistry bulk lithium loss from the positive electrode resulted in accumulation of lithium in the negative electrode [11,12].

Modern electrolytes include molecules which undergo redox reactions at relatively low voltages, the products of which deposit on the negative or positive electrodes of LIBs [13–16]. The aggregation of reduced and oxidized products on the negative electrode is known as the SEI layer [17,18]. SEI layer formation is critical to device function as it inhibits exfoliation of bulk graphitic electrode, and continuous electrolyte breakdown, by preventing co-intercalation of solvent with Li^+ [19]. Continual SEI layer growth however, leads to capacity loss due to immobilization of lithium by irreversible electrochemical reactions [20]. In the case of electrolytes containing ethylene carbonate (EC), the SEI layer thickness reportedly grows with the square root of charge-discharge time [21,22].

Charge capacity loss in LIBs can be mitigated by the inclusion of passivating molecules with low reductive stability in the electrolyte [23–26]. One of the best performing and most economical molecules with low reductive stability is vinylene carbonate (VC). Madec et al. have measured thinner SEI layers, using x-ray photoelectron spectroscopy (XPS) on LIB negative electrodes

cycled in electrolytes containing VC and prop-1-ene-1,3-sultone (PS) additives after cycling, as compared to baseline electrolytes containing EC [13]. Dedryvère validated the notion that the pi bond of VC allowed for facile polymerization of the SEI forming molecule using XPS [27,28].

Despite the effort to effectively attribute capacity loss to particular mechanistic origins, and efforts to develop accurate capacity loss models, few direct quantifications of lithium distribution as a function of cell age and materials exist. As a result, there are few charge capacity loss models dependent on true materials states. Accurate and direct accounting of lithium immobilization in the SEI and loss from the positive electrode of this kind has largely been impeded due to the dearth of suitable characterization techniques.

Efforts to directly quantify lithium inventory in LIBs include microscopic efforts [29], utilization of ion coupled plasma and glow discharge-optical emission spectroscopy (ICP/GD-OES) [30–32], neutron beam analysis [33], time of flight secondary ion mass spectroscopy (TOF-SIMS) [34] and lithium-nuclear reaction analysis (Li-NRA) [35–37]. Sunitha et al. evaluated the ^{7}Li (p, γ)^{8}Be nuclear reaction for depth profiling $LiCoO_2$ and graphite and found the concentration accuracy to within 0.2 at.% [35]. We recently performed the first high depth resolution profiles of the negative electrode using the same reaction and found accurate quantification with the SEI layer and beyond as a function of state of charge (SOC) and state of health (SOH) in $LiCoO_2$/graphite systems [36].

In this work we analyze the distribution of lithium in the SEI layer and bulk positive electrode in aged LIBs as a function of electrolyte composition, cycle number, and cycling time using Li-NRA. NRA techniques have previously been utilized for the study of LIB systems [38–40]. Recently Gonzalez-Arrabal et al. characterized two similar ion beam techniques for mesoscale characterization of positive electrode material [41].

2. Experimental

2.1. Electrolyte formulations

All electrolyte formulations contained 1 M $LiPF_6$ (BASF). We compared performance of 3 wt.% VC (98%, Sigma Aldrich) added to DMC (anhydrous, <15 ppm H_2O, Sigma Aldrich) with 50 wt.% ethylene carbonate (EC, anhydrous, <15 ppm H_2O, Sigma Aldrich) 50 wt.% DMC. The two electrolyte formulations are referred to as **3% VC** and **Control** respectively moving forward.

2.2. Cell description and preparation

Machine manufactured, 180 mAh $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ (NMC 442)/artificial graphite dry cells balanced for 4.35 V were obtained from Li-Fun Technology, China. The materials and microstructural information of these cells are available in Xia et al. [23].

The cells were opened, and vacuum dried at −30 kPa vs atmosphere and 80 °C for 18 h before transferring to a VAC glovebox maintained at O_2 and H_2O levels below 0.2 ppm and 0.5 ppm respectively. Each pouch cell was filled with 0.9 g of electrolyte. The cells were then double evacuated in a chamber style vacuum sealer at −0.8 MPa before sealing. After vacuum sealing, the cells were transferred to an environmental chamber set to 40 °C. Initially, cells were charged at 2 mA to 1.5 V and held at 1.5 V for 24 h to ensure electrolyte wetting, and then charged at a rate of C/20 (9 mA) to 3.5 V to aid conformal SEI formation. The cells were opened in the glovebox to remove excess gas formed during the SEI formation step, and re-vacuum sealed. The cells were then transferred back into the environmental chamber at 40 °C and charged at C/20 to 4.2 V and then discharged at C/20 to 2.8 V for the

first cycle post SEI formation. Long term cycling was performed between 4.2 V and 2.8 V, at C/3 (60 mA) on Arbin BT2453 cycler. Data, was rapidly extracted from Arbin *.res files using custom Python scripts. Use of these specific pouch cells and cycling procedure reproduced the methods of Xia et al. and Madec et al. using distinct electrolyte formulation [23,42].

After completion of cycling, the pouch cells were disassembled in the glovebox, and electrode material extracted from an identical location for all samples. The electrode material was double rinsed with DMC for 1 h, dried in argon atmosphere at room temperature, and subsequently sealed in an air tight container prior to ion beam experiments.

2.3. Lithium nuclear reaction analysis

Lithium nuclear reaction analysis (Li-NRA) of negative electrode was performed as per the nuclear reaction ^{7}Li (p, γ)^{8}Be with resonance energy (E_{Li-res}) of 441 KeV. The incident beam energy was varied between 430 keV and 550 keV in 3 keV step size, and the resulting γ-rays intensity was collected until accumulation of 1.0 μC of beam current. Depth profiling of positive electrodes were performed at 3 keV step size up to 500 keV energy, and beyond that the step size was increased to 20 keV for faster depth profiling.

Depth profiling was performed at the Ion Beam Lab at SUNY Albany. Details of the facility and technique are available in Lanford et al. [43,44]. The details of modeling methodology for converting the raw γ-ray intensity versus beam energy to Li at.% versus depth are provided in Schulz et al. [36].

3. Results and discussion

3.1. Electrochemical data

Differential capacity analysis (dQ/dV versus V) of the formation cycle (charged at C/20 rate) for 3% VC, Control electrolyte and 1 M $LiPF_6$ in DMC as reference are shown in Fig. 1. The observed peaks are indicative of quantity of electrochemical reaction and electrolyte thermodynamic stability as a function of applied potential. A large peak at 3.1 V and subsequent peak at 3.3 V is observed for 1 M $LiPF_6$ in DMC which we attribute to DMC reduction. This peak occurs at a similar voltage as peaks attributed to reduction of ethyl methyl carbonate (EMC) under near identical conditions [45]. This is despite DMC having been simulated in electrolyte to have greater stability than EMC [46]. Addition of 3 wt. % VC to DMC completely suppresses the reduction peak of DMC. Introduction of 50% EC to DMC also suppresses the peak associated with DMC though additional current is consumed during the formation of the SEI. The lower thermodynamic stability of VC and EC lead to their preferential breakdown during the formation cycle [23,42]. Comparison of discharge capacity versus cycle number for 3% VC and 50% EC or Control electrolyte (Fig. 1b) shows a well characterized steeper reduction in charge capacity retention for Control electrolyte.

Voltage versus capacity plots of cells with Control electrolyte (Fig. 2a), terminally cycled to 1 formation cycle (C/20), 10, 50 and 106C/3 cycles, demonstrate the decreasing nominal voltage and reduced capacity resulting from prolonged cycling. Cells containing 3% VC electrolyte were terminated at 1, 100 and 200 cycles (Fig. 2b) and showed significant improvements in nominal voltage and capacity retention over Control electrolyte.

The study comprises of eight cells, produced in an identical manner but stopped and analyzed after cycling for different number of hours (Table 1).

Cells with either electrolyte were analyzed after electrode wetting (1.5 V, 24 h, 40 °C) but before SEI formation to serve as representative of background reporting. Additionally formation