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Effect of overcharge on $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$ cathodes: NMP-soluble binder. II — Chemical changes in the anode

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HIGHLIGHTS

- Cells were systematically overcharged and the resulting components, characterized.
- Cathode metals were found in anode; their concentrations increased with state-of-charge.
- Anode surface chemistry indicates a mixture of $LiF:LiPO_3$ and organophosphates.
- The area ratio of the two of the organophosphates tended to a steady state with SOC.

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ABSTRACT

Cells based on nickel manganese cobalt oxide (NMC)/graphite electrodes, which contained polyvinylidene difluoride (PVDF) binders in the electrodes, were systematically charged to 100, 120, 140, 160, 180, and 250% state of charge (SOC). Characterization of the anodes by inductively-coupled-plasma mass spectrometry (ICP-MS), X-ray photoelectron spectroscopy (XPS), and high-performance liquid chromatography coupled with electrospray ionization mass spectrometry (HPLC-ESI-MS) showed several extent-of-overcharge-dependent trends. The concentrations (by wt) of nickel, manganese, and cobalt in the negative electrode increased with SOC, but the metals remained in the same ratio as that of the positive. Electrolyte reaction products, such as $LiF:LiPO_3$, increased with overcharge, as expected. Three organic products were found by HPLC-ESI-MS. From an analysis of the mass spectra, two of these compounds seem to be organophosphates, which were formed by the reaction of polymerized electrolyte decomposition products and PF_3 or $O{=}PF_3$. Their concentration tended to reach a constant ratio. The third was seen at 250% SOC only.

1. Introduction

A lithium-ion cell usually consists of a layered, lithiated transition-metal oxide as the cathode, an electrolyte, which is a mixture of organic carbonates and a lithium-bearing salt, and a graphite negative electrode. Probably the most important part of lithium-ion cells is the surface of the electrode. It affects the performance [1] and, possibly, the abuse response of the cell. In normal operation, the electrode reacts with the electrolyte, forming a passivating or solid electrolyte interphase (SEI) layer. At the positive electrode, the SEI layer consists of electrolyte oxidation products and, at the negative, electrolyte reduction products [2–4]. The structure and composition of the SEI is complex under normal operating conditions [5–9]. However, the changes in the SEI layers during overcharge are not well-understood. There are very few reports about what changes occur during the overcharge condition. Logically, one would expect that these changes would depend on the electrode binder and cell chemistry. Characterization of cells after overcharging would be very useful from the safety view point. The information gained may help mitigate the consequences of overcharge by telling us the nature of the SEI, how it changes during

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overcharge, and, possibly, how to increase its robustness.

Argonne National Laboratory (Argonne), Oak Ridge National Laboratory (ORNL), and Sandia National Laboratories (SNL) are collaborating to understand the physical and chemical changes on and in the electrodes that occur during cell abuse, such as during overcharge and overheating. The parameters in this study are the effects of the binder in the electrodes and of cell chemistry on the response of the cell to abusive conditions.

The first part of the study investigated the changes in the cell that were from the stepwise overcharge of $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$ (NMC532)/graphite cells made with the *N*-methylpyrrolidinone (NMP)-soluble binder, poly(vinylidene difluoride) (PVDF). Here, the cells were charged to 100–250% SOC (overcharged 0–150%). After overcharge, the cells were discharged to 0% SOC and taken apart in an argon-filled glovebox. These results were divided into three related papers, described below.

The first paper described the changes in the surface morphology of the anode. Here, scanning-electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) were used [10a]. In that study, the copper foil current collector under the anode layer displayed two sides; a dull side with exposed Cu grain boundaries and a smooth side with the typical microstructure of rolled copper. During cell disassembly, the anode layer exhibited more delamination from the collector on the shiny side (Fig. 1), most likely due to poor binder adhesion to the smooth surface.

In the first paper we found that, starting at 140% SOC, dendrites, such as those shown in Fig. 1, and transition metals were seen on the anode surface. Their concentrations increased with SOC. Additionally, their microstructure was very heterogeneous. In some places, it displayed a complex, layered structure.

This paper, the second in the series, provides a more detailed delineation of these surface materials and the bulk anode to further understand the chemical nature of the observed changes in the anode, the trends in these changes, and, possibly, the processes that led to them. Inductively-coupled-plasma mass spectrometry (ICP-MS), X-ray photoelectron spectroscopy (XPS), and high-performance liquid chromatography (HPLC) were used.

Finally, the third paper describes the changes at the cathode of these cells. Here, XPS, SEM, EDS, ^{6}Li nuclear magnetic resonance spectroscopy, and X-ray diffraction analysis of the cathodes indicated the formation of a thin, carbon- and oxygen-rich interfacial layer on the cathode surface and lithium loss above 140% SOC. However, the layered crystal structure was retained throughout the experiment [10b].

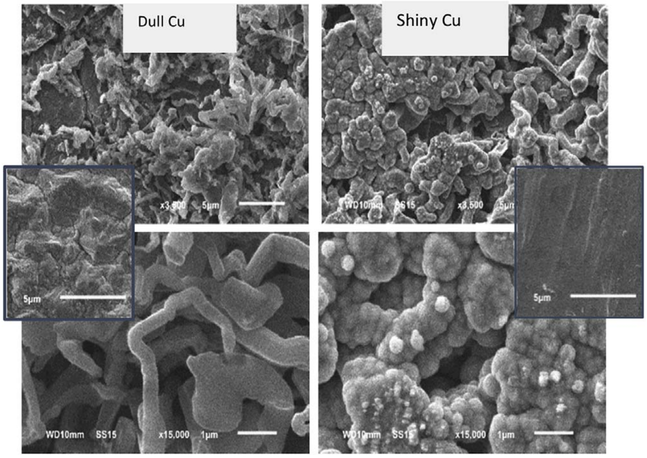

Fig. 1. The insets show the surface morphologies of the copper foil under the graphite layer. Well-defined copper grains were seen on the dull side; grain boundaries were not obvious on the shiny side. The larger images show the surface morphologies on an anode taken from a cell overcharged to 140% SOC. The morphology of the dull side consisted of cylindrical, dendrite-like structures. The structures on the shiny side were nodular (from Ref. 9a).

2. Experimental

Materials. 1.5-Ah lithium-ion cells containing NMC532/graphite chemistry were fabricated, formed, and overcharged, as described in a previous publication [10a]. The rated capacity corresponded to about 55% of the theoretical amount of lithium in the oxide. The NMC532 cathode and graphite anode contained the NMP-soluble binder, PVDF. The negative-to-positive ratio was 1.1:1. With the exception of the outer two layers, all electrodes were double-sided. The electrolyte consisted of $1.2\,\underline{M}$ $LiPF_6$ in ethylene carbonate:diethylcarbonate (3:7 by wt). Further information is given in Ref. [10a].

3. Post-test characterization

As described earlier [10a], in an argon-filled glovebox, the cells were opened using ceramic scissors. The electrodes were removed from the separator ribbon and allowed to dry. Sections of the separator and positive and negative electrodes were cleaned by swirling them two times in excess dimethylcarbonate for 1 min each. After drying, the sections were characterized using elemental analysis, XPS, and HPLC.

ICP-MS. In the glovebox, the electrode coatings were scraped off the foils onto glassine paper using a spatula. Care was taken to keep the materials from each side of the anode laminate separate.

In the analysis process, each sample was first heated in air to burn off the carbon/organic components. For this step, a 100-mg portion of the sample material was transferred to a weighed quartz beaker (25 mL) and weighed. Then the beakers were placed in a laboratory furnace and heated in stages at 250, 500, and 700 °C. The temperature at each setting was held for several hours with at least four hours at 700 °C to ensure complete removal of graphitic carbon. The beakers were cooled in air.

The residue from ignition was dissolved by adding to the quartz beakers a small amount of water (enough to wet the residue), 3 mL Optima Grade HCl, and 2 mL Optima Grade nitric acid; covering the beaker with a watch glass; and heating under reflux. Each resulting solution was quantitatively transferred to a polypropylene centrifuge cone and diluted with water to 50 mL. The anode solutions were analyzed with a Perkin Elmer/Sciex ELAN DRC-II ICP-MS to determine concentrations of Ni, Mn, and Co, using either scandium or indium as the internal standard. The inductively coupled plasma mass spectrometer (ICP-MS) was calibrated with solutions prepared by diluting spectroscopic standards procured from Ultra Scientific, North Kingstown, RI. The mass fraction (μg/g) of each element in the anode material was calculated using the element concentration, the volume of solution in which the sample was dissolved, and the mass of sample taken. Uncertainty in the reported values is assigned as the larger of ± 1 μg/g or ± 6% of the reported value.

X-ray photoelectron spectroscopy (XPS). XPS of rinsed electrodes was conducted in a PHI 5000 VersaProbe II system from Physical Electronics with a base pressure of $\sim 2 \times 10^{-9}$ torr. The system was attached to the Ar- atmosphere glovebox and the samples were inserted into the XPS analysis chamber through the glovebox without exposure to ambient air. The spectra were obtained using an Al Kα radiation ($h\upsilon$ = 1486.6 eV) beam (100 μm, 25 W), with Ar+ and electron beam sample neutralization, in Fixed Analyzer Transmission mode with a pass energy of 11.75 eV. Shirley background subtraction and fitting to multiple Gaussian peaks were performed on all spectra using the Multipack software from Physical Electronics.

HPLC. Samples for HPLC analysis were prepared by scraping the anode coating (~40–70 mg) off the copper foil from the cells. Care was taken to keep the scrapings from the shiny and dull sides of the copper foil separate. The scrapings were placed in scintillation vials, then covered and removed from the glovebox. Approximately 1–1.5 mL of