Prospects for spinel-stabilized, high-capacity lithium-ion battery cathodes

CrossMark

Jason R. Croy [a, *], Joong Sun Park [a], Youngho Shin [b], Bryan T. Yonemoto [a], Mahalingam Balasubramanian [c], Brandon R. Long [a, 1], Yang Ren [c], Michael M. Thackeray [a]

[a] Electrochemical Energy Storage Department, Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA
[b] Energy Systems Division, Materials Engineering Research Facility, Argonne National Laboratory, Argonne, IL 60439, USA
[c] X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA

HIGHLIGHTS

- Layered lithium-metal-oxide cathode structures are stabilized by a spinel component.
- Pre-pilot scale optimization provides superior materials over lab-scale efforts.
- Surface treatment of spinel-stabilized cathodes improves cycling stability and rate.

ARTICLE INFO

ABSTRACT

Herein we report early results on efforts to optimize the electrochemical performance of a cathode composed of a lithium- and manganese-rich "layered-layered-spinel" (LLS) material for lithium-ion battery applications. Pre-pilot scale synthesis leads to improved particle properties compared with lab-scale efforts, resulting in high capacities (~200 mAh g^{-1}) and good energy densities (>700 Wh kg$_{oxide}^{-1}$) in tests with lithium-ion cells. Subsequent surface modifications give further improvements in rate capabilities and high-voltage stability. These results bode well for advances in the performance of this class of lithium- and manganese-rich cathode materials.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Lithium- and manganese-rich "layered-layered" (LL) cathode materials have been of significant interest for more than a decade due to the substantial capacity gains, improved safety, and lower cost compared with their layered counterparts. Generally denoted, in composite notation, as $xLi_2MnO_3 \cdot (1-x)LiMO_2$ (M = Mn, Ni, and Co), this class of electrode materials can deliver high capacities in lithium-ion cells, reaching 250 mAh g^{-1} and above [1–4]. However,

as is now well-known, these exceedingly high capacities come at the expense of structural stability, where the complex role of oxygen at high states of charge (SOC) leads to oxygen evolution, cation migration, and the irreversible transformation of local structures [5–16]. In particular, transition-metal-layer Li and $LiMn_6$ (Li_2MnO_3-type) ordering seems to play a key role in the observed magnitude of these phenomena. These degradation processes ultimately give rise to voltage fade and hysteresis and are likely also related, in part, to the poor rate performance typically observed for LL electrodes. Several reviews have recently been published on the details of voltage fade and hysteresis, as well as the associated structural considerations for this class of materials [8,10].

Voltage fade in layered oxides is characterized by an almost continuous decrease in the average voltage of cells and, consequently, their energy output with cycling [17]. Interestingly,

* Corresponding author. Argonne National Laboratory, 9700 South Cass Avenue, Bldg. 200, Lemont IL 60439-4837, USA.
E-mail address: croy@anl.gov (J.R. Croy).
[1] Current address: BASF Corp. 23800 Mercantile Road, Beachwood, OH 44122, USA.

capacity fade is not synonymous with voltage fade in that lithium- and manganese-rich LL materials can deliver anomalously high capacities (>250 mAh g^{-1}) despite the structural disorder induced by high voltage cycling [18,19]. This phenomenon may be related to current theories on disordered rock-salt cathodes [6]. While many strategies (e.g., coatings and dopants) have been proposed to reduce significantly this voltage fade, none thus far have been shown to stop or change the actual mechanisms involved with respect to a lithium- and manganese-based system [20,21]. Voltage fade is likely an inherent, bulk property of LL materials and is highly correlated to the local structures (including defects) that dictate, to a large extent, lithium site energies [10,22]. Following this line of thinking, we inferred that the idea of modifying local domain structures in the pristine materials might provide a viable path to mitigate the structural transformations and voltage fade in these electrodes during cycling. The final goal is to realize low-cost, manganese-rich cathodes capable of delivering high capacities while maintaining good structural stability and energy over long-term cycling. Specifically, while some nickel-rich, layered oxides can already deliver close to 200 mAh g^{-1} at slow rates, a more cost-effective, manganese-rich oxide that can compete with these more expensive options, without detrimental energy fade, is currently unavailable. Therefore, we have initiated a "bottom-up" strategy to achieve such a goal. By starting with lower lithium and manganese loadings, x, in $x\text{Li}_2\text{MnO}_3\cdot(1-x)\text{LiMO}_2$, and modifying local domains structures to mitigate the mechanisms of energy fade, a platform might be built toward the goal of practical, high-energy, lithium- and manganese-rich cathodes.

Thackeray et al. have been pursuing the strategy of embedding, in small concentration, small domains of a structurally compatible spinel component in the LL systems as a way to introduce stabilizing transition metal (TM) cations into the lithium layers [23,25]. This strategy offers several advantages: 1) the spinel structure contains a 3:1 mix of TMs to Li (and vice versa) in alternate layers, giving it an inherent stability against TM migration; 2) the three-dimensional nature of spinel structures allows for fast lithium-ion diffusion; 3) the working voltage of spinel-type cathodes can be tuned over a large voltage window, depending on composition [26–30]; 4) unoccupied octahedral sites of the pristine spinel structure can be used to help offset first-cycle irreversible capacity losses inherent to LL materials; and 5) spinel and layered structures are compatible and can be integrated at the nanoscale [31].

These attributes have been exploited to manipulate the local domain structure of LL materials and create complex "layered-layered-spinel" (LLS) electrodes, with promising results [23,24]. Several challenges associated with LLS electrodes, however, have yet to be overcome: 1) precise control over the final fraction of spinel-type domains incorporated into the final product; 2) control over domain composition; and 3) exacting detail of the actual local structures that ultimately form. With respect to 3), previous studies have shown that "spinel" concentrations above ~10–15% are easily identifiable by typical characterization methods such as X-ray diffraction (XRD), showing expected signatures. However, once the targeted concentration falls below 10%, bulk-averaged techniques are not suitable to accurately characterize changes in the local domain structure, and microscopic analyses like high-resolution transmission electron microscopy (TEM) might be the best way to study such samples. In addition, the exact nature of local structures that form may not necessarily have ideal $\text{Li}_{1+x}\text{M}_2\text{O}_4$-type, spinel configurations. For example, we have observed signatures resembling M_3O_4 spinel components with tetrahedral TMs leading to interesting electrochemical properties.

This result is evident in Fig. 1(a), which shows XRD patterns of a series of materials with increasing spinel content. Clearly visible at $2\Theta = {\sim}32°$, using a laboratory X-ray source, is the formation of a new peak as the spinel content increases. The position and intensity are consistent with the (220) plane of a cubic (Fd$\overline{3}$ m) M_3O_4 spinel, in which M is a transition metal (or metals) together with, or excluding lithium, as shown by the calculated XRD pattern ($a = 0.81333$ nm) in Fig. 1(a). In addition, the peaks broaden at $2\Theta = 36.5°$ (Fig. 1(b)) while the doublet at ~65° begins to merge as the spinel content increases, indicating the formation of a spinel component. Note that throughout the series, even when the spinel content is 26%, the superstructure peaks from the ordering of Li_2MnO_3-like domains ($2\Theta = 20-25°$) are observed, and that the expected "activation" plateau of the first-cycle charge is clearly visible in Fig. 1(c). These electrodes deliver stable capacities of ~180 mAh g^{-1}. Their excellent structural stability with cycling is highlighted in the dQ/dV plots of Fig. 1(c) for a LLS structure with a 13% spinel content.

Previous studies by Croy et al. aimed at controlling the TM content of lithium layers in LL cathodes have also shown promising results. For example, Fig. 2(a) shows in-situ, high-energy, synchrotron X-ray diffraction of a Li_2MnO_3 precursor treated in an acidic solution of nickel nitrate, as previously described [32]. The layered Li_2MnO_3 structure acts as a template into which nickel cations can be inserted by an ion-exchange-type process. Subsequent annealing drives the nickel into the structure and, depending on the final conditions (e.g., time and temperature of firing), the amount of nickel residing in the lithium layers of the final product can be tuned, as shown by the extended X-ray absorption fine structure (EXAFS) analysis of the coordination number in Fig. 2(b) for a nominal $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ cathode material. In addition, rock salt $\text{Li}_x\text{Ni}_{1-x}\text{O}$- and spinel LiM_2O_4-type structures can also be formed, dependent on synthesis conditions. These cathodes, despite having complex domain structures, have shown good performance [23,32,33]. Fig. 3(a)–(c) present the performance of the $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ electrode material when annealed at ~850 °C, at which the material is not yet fully layered, as shown in Fig. 2(a). Fig. 3(a) shows the excellent rate capability and capacity retention, while Fig. 3(b) and (c) show the good stability of the electrode during cycles 15–25, conducted after the rate test cycles shown in Fig. 3(a). The ultimate goal of the LLS strategy is, therefore, gaining control over cation occupancies within the lithium layers (octahedral or tetrahedral) to create local configurations that improve electrode cycling stability and performance.

Finally, lithium- and manganese-rich electrodes are known to undergo surface degradation when cycled to high voltages. This degradation can be mitigated by various surface treatments [20,34,35]. Therefore, any strategy to mitigate bulk structural changes will need to be coupled with surface protection strategies to maintain surface integrity, good rate performance, and minimal impedance rise with cycling.

Related to the synthesis of LLS materials, no extensive efforts have thus far been made to produce high-quality and robust electrode materials for electrochemical evaluation. While detailed characterization studies are still in progress, we highlight, herein, recent advances in developing lithium- and manganese-rich LLS electrodes via pre-pilot scale synthesis and surface treatments of a selected baseline LLS composition.

2. Experimental

2.1. Material synthesis

2.1.1. Oxalate co-precipitation

LLS materials were synthesized via several co-precipitation routes. TM oxalate co-precipitation was used for laboratory-scale synthesis because of the excellent reproducibility when these precursors are used. $\text{Mn}_{0.53125}\text{Ni}_{0.28125}\text{Co}_{0.1875}\text{C}_2\text{O}_4\cdot2\text{H}_2\text{O}$