

Short communication

Chemical and structural instabilities of lithium ion battery cathodes

A. Manthiram*, J. Choi

Materials Science and Engineering Program, The University of Texas at Austin, Austin, TX 78712, United States

Available online 30 May 2006

Abstract

The chemical and structural stabilities of various layered $\text{Li}_{1-x}\text{Ni}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ cathodes are compared by characterizing the samples obtained by chemically extracting lithium from the parent $\text{Li}_{1-x}\text{Ni}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ with NO_2BF_4 in an acetonitrile medium. The nickel- and manganese-rich compositions such as $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ exhibit better chemical stability than the LiCoO_2 cathode. While the chemically delithiated $\text{Li}_{1-x}\text{CoO}_2$ tends to form a P3 type phase for $(1-x) < 0.5$, $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ maintains the original O3 type phase for the entire $0 \leq (1-x) \leq 1$ and $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ forms an O1 type phase for $(1-x) < 0.23$. The variations in the type of phases formed are explained on the basis of the differences in the chemical lithium extraction rate caused by the differences in the degree of cation disorder and electrostatic repulsions. Additionally, the observed rate capability of the $\text{Li}_{1-x}\text{Ni}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ cathodes bears a clear relationship to cation disorder and lithium extraction rate.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Lithium ion batteries; Layered oxides; Chemical stability; Crystal chemistry; Rate capability

1. Introduction

Layered LiCoO_2 is used as the cathode presently in most of the lithium ion cells due to its easy synthesis and excellent reversible lithium extraction/insertion properties. However, it could be used only in the range of $0.5 \leq (1-x) \leq 1$ in $\text{Li}_{1-x}\text{CoO}_2$, limiting its practical capacity to 140 mAh g^{-1} (50% of theoretical capacity). Also, Co is relatively expensive and toxic. These difficulties have generated enormous interest in the design and development of alternative cathode hosts. In this regard, layered $\text{LiNi}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ cathodes have become appealing recently as they offer higher capacity, lower cost, and enhanced safety compared to the conventional LiCoO_2 cathode [1–6]. For example, $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ have been reported to offer higher reversible capacities of $160\text{--}200 \text{ mAh g}^{-1}$ (60–70% of theoretical capacity) [3,4]. However, the reason for the wide variations in the capacities of the layered oxide compositions is not fully established in the literature. The lack of such an understanding is due to the fact that most of the studies have concentrated on both the in situ and ex situ structural characterization of the electrochemically charged $\text{Li}_{1-x}\text{MO}_2$ ($M = \text{Mn, Ni, and Co}$) cathodes. Consider-

ing the highly oxidized nature of the $\text{M}^{3+/4+}$ redox couples and a near equivalence of the $\text{M}^{3+/4+} : 3d$ and $\text{O}^{2-} : 2p$ energies, chemical instabilities resulting in an oxidation of O^{2-} ions at deep charge or ion exchange with protons could play a role in limiting the reversible capacities of layered oxide cathodes. To address this issue, our group has been focusing on a systematic investigation of the structural and chemical characterization of a number of chemically delithiated $\text{Li}_{1-x}\text{MO}_2$ compositions and a correlation of the findings to the electrochemical performances. We present here an overview of the results and the salient features.

2. Experimental

The layered oxide cathodes were synthesized as reported elsewhere [6–17] either by standard solid state reactions or by reacting lithium hydroxide with the coprecipitated hydroxides of the other metal ions at $700\text{--}900^\circ\text{C}$ for 24 h; some compositions such as $\text{LiNi}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ were prepared with 7 at.% excess lithium [6,14–17]. Chemical extraction of lithium was carried out by stirring the LiMO_2 powders in an acetonitrile solution of NO_2BF_4 under argon atmosphere using a Schlenk line, followed by washing the products formed several times with acetonitrile under argon atmosphere to remove LiBF_4 , drying under vacuum at ambient temperature, and storing in an argon-filled glove box to avoid reaction with the ambient.

* Corresponding author. Tel.: +1 512 471 1791; fax: +1 512 471 7681.
E-mail address: rmanth@mail.utexas.edu (A. Manthiram).

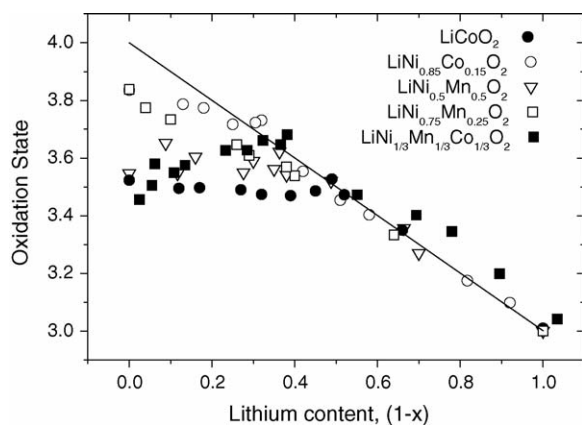


Fig. 1. Comparisons of the variations of the average oxidation state of the transition metal ions with lithium content $(1-x)$ in $\text{Li}_{1-x}\text{Ni}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$. The solid line refers to the theoretically expected oxidation state.

The samples were characterized by X-ray diffraction and the structural refinements and lattice parameter determinations were carried out with the Rietveld method using the DBWS-9411 PC program [18]. Lithium contents were determined by atomic absorption spectroscopy and the average oxidation state of transition metal ions was determined by iodometric titration [19]. Electrochemical performances were assessed with CR2032 coin cells assembled with the cathode (75 wt.% active material, 20 wt.% acetylene black, and 5 wt.% PTFE binder), lithium anode, and 1 M LiPF_6 in ethylene carbonate (EC)/diethyl carbonate (DEC) electrolyte.

3. Results and discussion

3.1. Chemical instability

Fig. 1 compares the variations of the average oxidation state of the transition metal ions with lithium content $(1-x)$ in the chemically delithiated $\text{Li}_{1-x}\text{Ni}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ samples that were obtained by stirring for 2 days the parent $\text{LiNi}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ oxide powders with an acetonitrile solution containing various amounts of NO_2BF_4 [10,11,14,15]. While the oxidation state of cobalt in the $\text{Li}_{1-x}\text{CoO}_2$ system deviates from the theoretically expected value (solid line) and remains constant for $(1-x) < 0.5$, the average oxidation state of

the transition metal ions in the other systems in Fig. 1 deviates from the theoretical value at a lower lithium content of 0.3–0.4. The charge compensation during lithium extraction while the oxidation state deviates from the theoretical value could be accommodated by either a loss of oxygen from the lattice or an exchange of lithium ions by protons from the reaction medium. While an ion exchange by protons may be preferred if enough protons are present, a loss of oxygen from the lattice could occur in the absence of protons as may be the case in the actual lithium ion cells. Either situation (ion exchange by protons or oxygen loss) may reflect the onset of chemical instability in the system. Thus, the chemical delithiation experiments serve as a tool to assess the relative chemical stability of the layered LiMO_2 cathodes with various transition metal ions. The deviation of the oxidation state from the theoretical value at a higher lithium content $(1-x) < 0.5$ in LiCoO_2 compared to that in the Ni- and Mn-rich systems $((1-x) < 0.4)$ in Fig. 1 implies a worse chemical stability for the LiCoO_2 system and consequently a lower reversible capacity.

The differences in the relative chemical stability in the $\text{Li}_{1-x}\text{Ni}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ systems can be understood by considering the qualitative band diagram in Fig. 2 and the electronic structure. In the case of LiCoO_2 with a $\text{Co}^{3+}:3d^6$ configuration, the t_{2g} band is completely filled and the e_g band is empty. As lithium is extracted from LiCoO_2 , the Co^{3+} ions are oxidized to Co^{4+} , which is accompanied by a removal of electrons from the t_{2g} band. Since the t_{2g} band overlaps significantly with the top of the $\text{O}^{2-}:2p$ band, deeper lithium extraction with $(1-x) < 0.5$ in $\text{Li}_{1-x}\text{CoO}_2$ may result in a removal of electrons from the $\text{O}^{2-}:2p$ band as well. The removal of a significant amount of electrons from the $\text{O}^{2-}:2p$ band will result in an oxidation of O^{2-} ions and an ultimate loss of oxygen from the lattice. Alternatively, if sufficient protons are present in the reaction medium, then the chemical instability may be overcome by an ion exchange of lithium by protons without involving a loss of oxygen from the lattice. In contrast, the LiNiO_2 and LiMnO_2 systems with $\text{Ni}^{3+}:3d^7$ and $\text{Mn}^{3+}:3d^4$ configurations involves removal of electrons only from the e_g band, which either barely overlaps with or lies well above the $\text{O}^{2-}:2p$ band, and therefore they have a better chemical stability than the LiCoO_2 system. Thus, we believe the higher reversible capacities realized with the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ systems compared to that with the LiCoO_2 system is due to a better chemical stability.

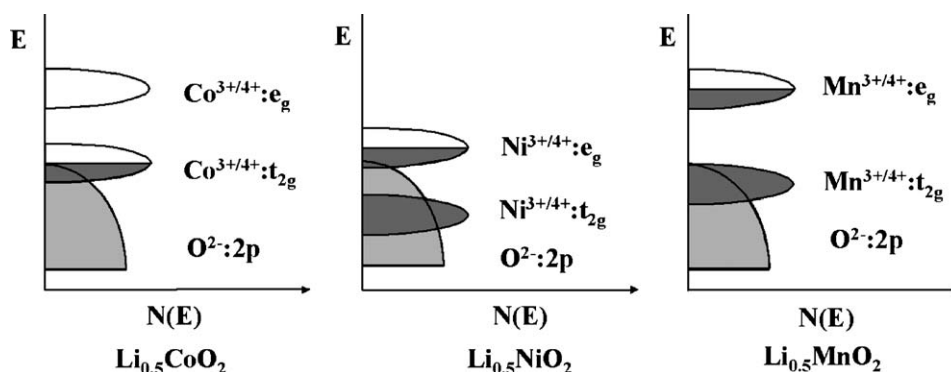


Fig. 2. Comparison of the band diagrams of $\text{Li}_{0.5}\text{CoO}_2$, $\text{Li}_{0.5}\text{NiO}_2$, and $\text{Li}_{0.5}\text{MnO}_2$.

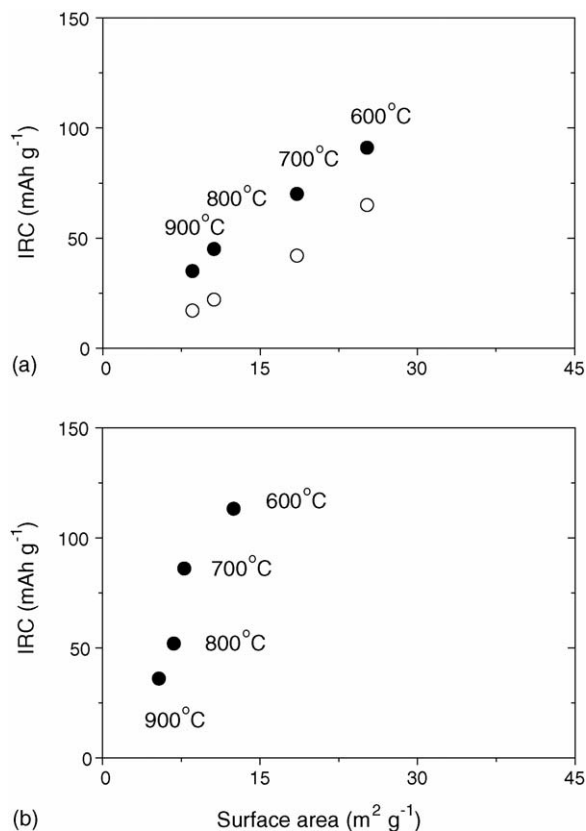


Fig. 3. Relationship between irreversible capacity (IRC) loss and BET surface area of: (a) $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and (b) LiCoO_2 cathodes. The open and closed symbols refer, respectively, to 3.0–4.3 and 3.0–4.6 V at a slow rate of $C/100$.

To illustrate further the importance of the differences in the chemical instability, we have compared the irreversible capacity (IRC) losses of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and LiCoO_2 synthesized at various temperatures (Fig. 3) [14]. The IRC exhibits a linear relationship to the BET surface area, suggesting that parasitic electrochemical reactions such as the oxidation of electrolyte occurring on the cathode surface may contribute to IRC analogous to the reduction of electrolyte occurring on the graphite anode surface, producing SEI layers [20–22]. The data indicate that the IRC per unit area (slope of the linear relationship in Fig. 3) for LiCoO_2 (10.55 mAh m^{-2} at 3–4.6 V) is much higher than that found for $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (3.30 mAh m^{-2}) in the same voltage range. This could be due to the greater chemical instability of the $\text{Li}_{1-x}\text{CoO}_2$ cathode with $(1-x) < 0.5$ and the consequent enhanced reactivity with the electrolyte compared to that for the $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathodes.

3.2. Structural instability

Fig. 4 shows the evolution of the X-ray diffraction patterns with the lithium content $(1-x)$ for the chemically delithiated $\text{Li}_{1-x}\text{CoO}_2$, $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$, and $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ [10,11,15]. While the $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ system maintains the parent O3 type structure without the formation of any new phases for the entire lithium content ($0 \leq (1-x) \leq 1$), the $\text{Li}_{1-x}\text{CoO}_2$ and $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ systems begin to form, respec-

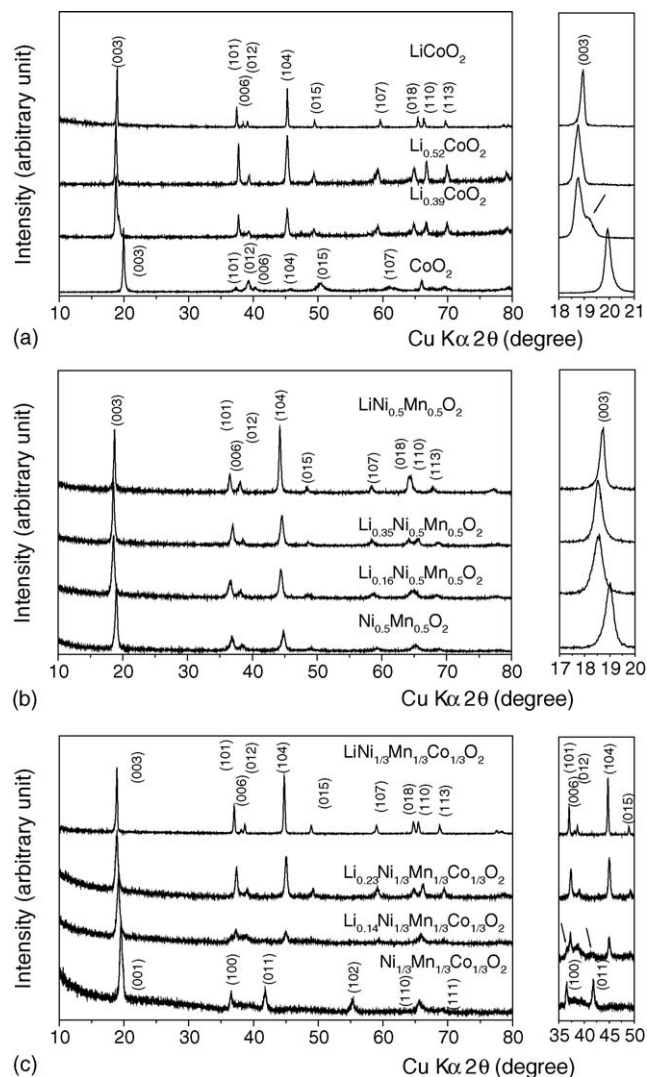


Fig. 4. X-ray diffraction patterns of the: (a) $\text{Li}_{1-x}\text{CoO}_2$, (b) $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$, and (c) $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ ($0 \leq (1-x) \leq 1$) samples obtained by chemically extracting lithium from $\text{Li}_{1-x}\text{Ni}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ with NO_2BF_4 for 2 days.

tively, a new P3 type phase for $(1-x) < 0.5$ and O1 type phase for $(1-x) < 0.23$. The P3 and O1 type phases having an oxygen stacking sequence along the c -axis of, respectively, AABBC and ABABAB are formed by a gliding of the MO_2 sheets in the original O3 type phase having an oxygen stacking sequence of ABCABC [23].

In order to understand the factors controlling the formation of different structures for the chemically delithiated phases, we have focused on the cation disorder between the lithium and transition metal planes and the chemical lithium extraction rate. Fig. 5a compares the lithium contents remaining in $\text{Li}_{1-x}\text{Ni}_{0.5-y}\text{Mn}_{0.5-y}\text{Co}_y\text{O}_2$ after 15 min of chemical lithium extraction reaction with 100% excess oxidizer NO_2BF_4 in acetonitrile medium. The lithium content $(1-x)$ remaining in $\text{Li}_{1-x}\text{Ni}_{0.5-y}\text{Mn}_{0.5-y}\text{Co}_y\text{O}_2$ increases with decreasing Co content in the region of $0.15 < 2y \leq 1.0$ and remains nearly constant at low Co contents of $0 \leq 2y < 0.15$, indicating a faster lithium extraction rate with increasing Co content $2y$. Interestingly, the lithium extraction rate bears a relationship to the % cation dis-

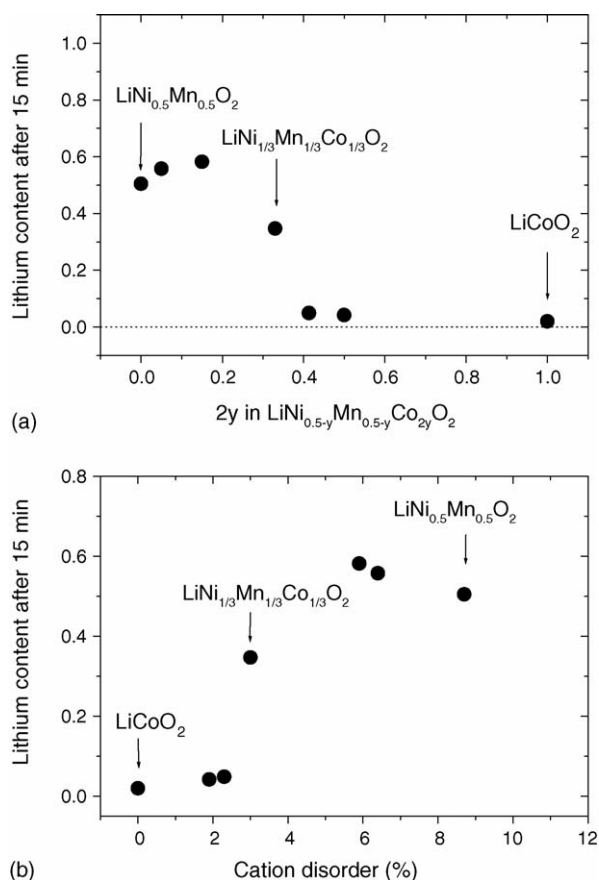


Fig. 5. Variations of the lithium contents remaining after 15 min of chemical lithium extraction reaction of the layered $\text{LiNi}_{0.5-y}\text{Mn}_{0.5-y}\text{Co}_{2y}\text{O}_2$ with NO_2BF_4 in acetonitrile medium with: (a) Co content $2y$ and (b) % cation disorder.

order determined by Rietveld analysis of the X-ray diffraction data as seen in Fig. 5b. The lithium extraction rate decreases as the degree of cation disorder increases. Thus, a faster lithium extraction due to a good cation ordering in the $\text{Li}_{1-x}\text{CoO}_2$ system (high Co content) results in the formation of the metastable P3 type phase, while a moderately slow lithium extraction due to some cation disorder in the $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ system (intermediate Co content) leads to the stabilization of the thermodynamically more stable O1 type phase [12]. On the other hand, a significant amount of cation disorder present in the $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ system (no Co content) prevents the formation of O1 and P3 type phases from the initial O3 type structure because of the electrostatic repulsion between the M^{n+} cations present in the lithium and transition metal planes across the shared polyhedral faces of the O1 and P3 type structures [13]. Additionally, any proton incorporated into the lattice from the chemical delithiation medium could also play a role on the type of phases formed.

To illustrate the influence of the lithium extraction rate on the crystal chemistry of the phases formed, we have also compared the structures of the fully delithiated phases formed from $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ synthesized at various temperatures (Fig. 6) [17]. With increasing synthesis temperature, the structure of the delithiated phase changes from a single P3 type phase

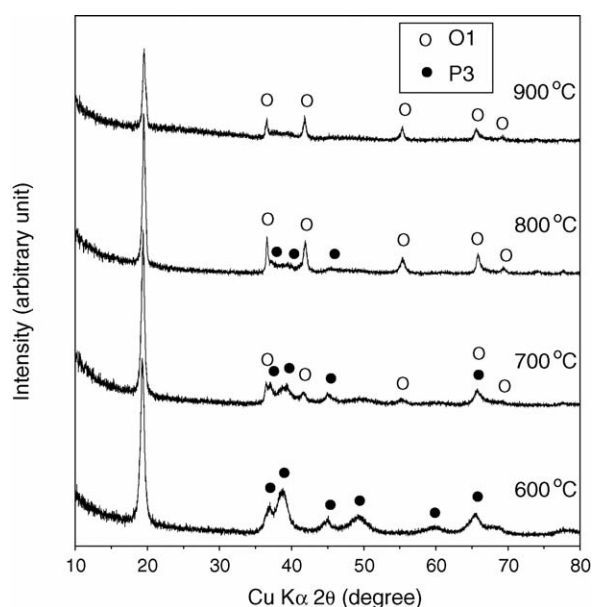


Fig. 6. Comparison of the X-ray diffraction patterns of the delithiated $\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ obtained by reacting with NO_2BF_4 for 2 days the $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ samples synthesized at various temperatures (600–900 °C).

(600 °C) to a single O1 type phase (900 °C), with both the O1 and P3 phases coexisting for the intermediate synthesis temperatures (700 and 800 °C). While a faster lithium extraction rate with the samples synthesized at lower temperatures due to a larger surface area (Fig. 3) and smaller particle size resulting in a shorter lithium diffusion distance leads to the formation of the metastable P3 type phase, a moderate lithium extraction rate with the sample synthesized at higher temperatures leads to the formation of the thermodynamically more stable O1 type phase.

3.3. Rate capability

Although $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ exhibit higher reversible capacities than LiCoO_2 , they show lower rate capability compared to LiCoO_2 as seen in Fig. 7a. For example, while LiCoO_2 retains 90% of its capacity on going from $C/10$ to $4C$ rate, $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ retain, respectively, 75% and 45% [16]. The rate capabilities were evaluated by first charging the cathodes at $C/10$ rate and then discharging at various rates ($C/10$ to $4C$ rate) between 4.3 and 3.0 V. The monotonic decrease in rate capability with decreasing Co content is due to the increasing cation disorder as seen in Fig. 7b and the consequent decrease in the lithium extraction rate (Fig. 5b). We believe that the presence of a considerable amount of transition metal ions in the lithium layer in the nickel-rich $\text{LiNi}_{0.5-y}\text{Mn}_{0.5-y}\text{Co}_{2y}\text{O}_2$ samples impedes the lithium diffusion, resulting in a slower chemical lithium extraction rate and lower electrochemical discharge rate. This conclusion is supported further by the fact that the rate capability with a given Co content increases on improving the cation ordering by employing an oxygen-rich synthesis atmosphere [16]. Although variations in electrical conductivity could also influence the electrochemical rate capability, we could not find

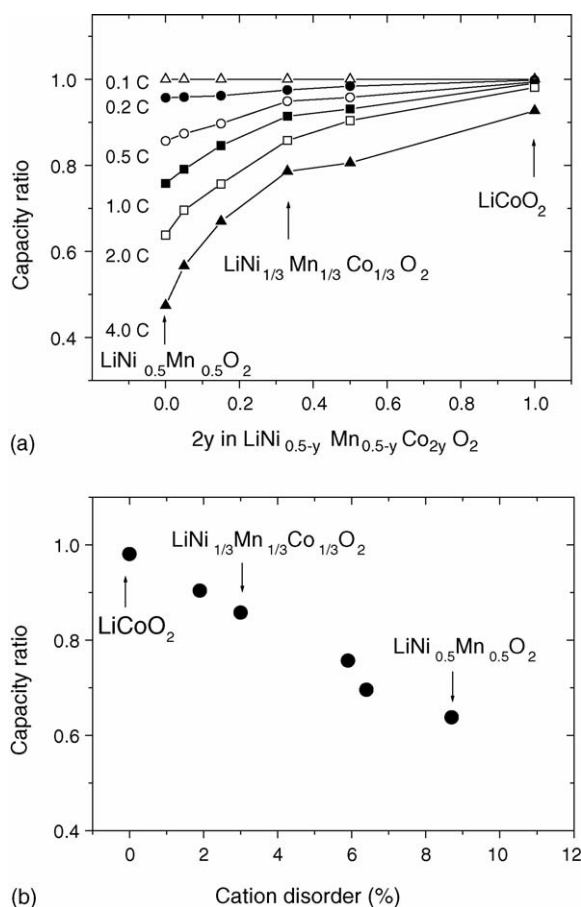


Fig. 7. (a) Comparison of the rate capabilities of the $\text{LiNi}_{0.5-y}\text{Mn}_{0.5-y}\text{Co}_{2y}\text{O}_2$ cathodes with various Co contents $2y$ (the capacity ratio values were obtained by dividing the capacity at various C rates by the capacity at 0.1C rate) and (b) correlation of the rate capability to % cation disorder in $\text{LiNi}_{0.5-y}\text{Mn}_{0.5-y}\text{Co}_{2y}\text{O}_2$ (the capacity ratio values were obtained by dividing the capacity at 2C rate by that at 0.1C rate).

any clear relationship between the observed rate capability and electrical conductivity.

4. Conclusions

Chemical instabilities arising from an overlap of the $\text{M}^{3+/4+}:3d$ band with the top of the $\text{O}^{2-}:2p$ band and the consequent tendency to lose oxygen from the lattice or incorporate protons from the medium play a critical role in controlling the reversible capacity limits of layered $\text{LiNi}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ cathodes. The higher capacities of the recently developed $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathodes ($160\text{--}200\text{ mAh g}^{-1}$) compared to the LiCoO_2 cathode

(140 mAh g^{-1}) is due to a better chemical stability. Additionally, the chemical lithium extraction rate, which in turn is controlled by the degree of cation disorder, is found to influence the formation of O3 versus P3 versus O1 type structures for the delithiated phases and the electrochemical rate capability. Our future experiments will focus on delineating ion exchange by protons versus oxygen loss at deep lithium extraction by employing prompt gamma-ray activation analysis to quantitatively determine the proton contents in chemically and electrochemically delithiated samples.

Acknowledgments

Financial support by the NASA Glenn Research Center, Office of FreedomCAR and Vehicle Technologies of the U.S. Department of Energy under Contract no. DE-AC03-76SF00098 (Subcontract no. 6712770), and Welch Foundation grant F-1254 is gratefully acknowledged.

References

- [1] Z. Liu, A. Yu, J.Y. Lee, J. Power Sources 81–82 (1999) 416.
- [2] M. Yoshio, H. Noguchi, J. Itoh, M. Okada, T. Mouri, J. Power Sources 90 (2000) 176.
- [3] T. Ohzuku, Y. Makimura, Chem. Lett. (2001) 642.
- [4] Z. Lu, D.D. Macneil, J.R. Dahn, Electrochem. Solid State Lett. 4 (2001) A191.
- [5] N. Yabuuchi, T. Ohzuku, J. Power Sources 119–121 (2003) 171.
- [6] J. Choi, A. Manthiram, Electrochem. Solid State Lett. 7 (2004) A365.
- [7] R.V. Chebiam, F. Prado, A. Manthiram, Chem. Mater. 13 (2001) 2951.
- [8] R.V. Chebiam, F. Prado, A. Manthiram, J. Solid State Chem. 163 (2002) 5.
- [9] S. Venkatraman, A. Manthiram, Chem. Mater. 14 (2002) 3907.
- [10] S. Venkatraman, Y. Shin, A. Manthiram, Electrochem. Solid State Lett. 6 (2003) A9.
- [11] S. Venkatraman, A. Manthiram, Chem. Mater. 15 (2003) 5003.
- [12] S. Venkatraman, J. Choi, A. Manthiram, Electrochem. Commun. 6 (2004) 832.
- [13] S. Venkatraman, A. Manthiram, Solid State Ionics 176 (2005) 291.
- [14] J. Choi, A. Manthiram, Electrochem. Solid State Lett. 8 (2005) C102.
- [15] J. Choi, A. Manthiram, J. Electrochem. Soc. 152 (2005) A1714.
- [16] J. Choi, A. Manthiram, Solid State Ionics 176 (2005) 2251.
- [17] J. Choi, A. Manthiram, J. Mater. Chem. 16 (2006) 1734.
- [18] R.A. Young, A. Shakhivel, T.S. Moss, C.O. Paiva Santos, J. Appl. Crystallogr. 28 (1995) 366.
- [19] A. Manthiram, J.S. Swinnea, Z.T. Sui, H. Steinfink, J.B. Goodenough, J. Am. Chem. Soc. 109 (1987) 6667.
- [20] D. Aurbach, M.D. Levi, E. Levi, H. Teller, B. Markovsky, G. Salitra, J. Electrochem. Soc. 145 (1998) 3024.
- [21] D. Aurbach, B. Markovsky, M.D. Levi, E. Levi, A. Schechter, M. Moshkovich, Y. Cohen, J. Power Sources 81–82 (1999) 95.
- [22] D. Aurbach, J. Power Sources 89 (2000) 206.
- [23] C. Delmas, C. Fouassier, P. Hagenmuller, Physica 99B (1980) 81.