

Short communication

Thermal behavior of delithiated $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ powders[☆]

Ilias Belharouak^{*}, Wenquan Lu, Jun Liu, Donald Vissers, Khalil Amine

Chemical Engineering Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA

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Abstract

The hybrid pulse power characteristics (HPPC) of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ electrode materials have been evaluated according to the FreedomCAR test manual and found to meet the power requirements for HEV applications. In addition to its excellent power capability, $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ electrode material has shown much better safety characteristics than the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrode material. To investigate the reason for this finding, $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ powders were chemically delithiated using NO_2BF_4 oxidizer in an acetonitrile medium. The thermal gravimetric results show that both $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ obtained powders release oxygen starting from 190 and 250 °C with an overall oxygen loss of 11 and 6 wt% at 600 °C, respectively. The reactivity of the delithiated powders with several electrolytes was studied by differential scanning calorimetry (DSC) and accelerated rate calorimetry (ARC) techniques. The relationship between the safety characteristics of $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powders and their thermal stability was discussed in light of their structural rearrangement during thermal heating.

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1. Introduction

$\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ oxide is a potential positive active electrode for application in batteries for hybrid electric vehicles (HEVs) because of its outstanding power characteristics [1,2]. Therefore, extensive work has been carried out at Argonne National Laboratory to investigate the thermal behavior of the fully charged $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ powder in the presence of selected solvents, salt and binders [3,4]. The thermal abuse tolerance study shows that this system generates a large amount of oxygen—enough to lead to major reactions inside a Li-ion cell in the case of overcharge and/or temperature rise of the cell under operational conditions. Because of the safety hazards associated with lithium-ion batteries,

there is a need to search for a cathode that has better safety characteristics and that could replace $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ without sacrificing the power characteristics needed for use in HEV applications [5]. To this end, the low-nickel content $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ electrode material was found to not only meet and exceed the power requirements for the HEV application, but also to have much better safety characteristics than the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrode [6]. The present paper reports on the thermal and structural stability of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ powders after being subjected to chemical delithiation using a NO_2BF_4 oxidizer. The general safety characteristics of the delithiated powders are discussed based on the correlation between the oxygen release and the structural transformation during the heat treatment of these active materials.

2. Experimental

Chemical delithiation [7,8] of the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ materials was achieved by stirring the powders in acetonitrile solutions containing NO_2BF_4 oxidizer in excess. After 24 h of lithium extraction at room temperature, the solutions were filtered and the remaining

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^{*} Corresponding author.

E-mail address: belharouak@cmt.anl.gov (I. Belharouak).

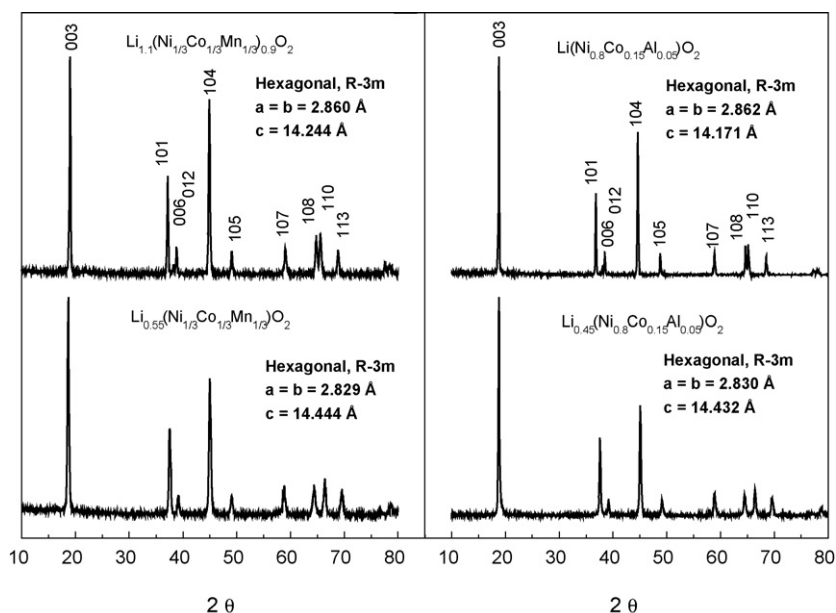


Fig. 1. XRD patterns before and after delithiation of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ materials.

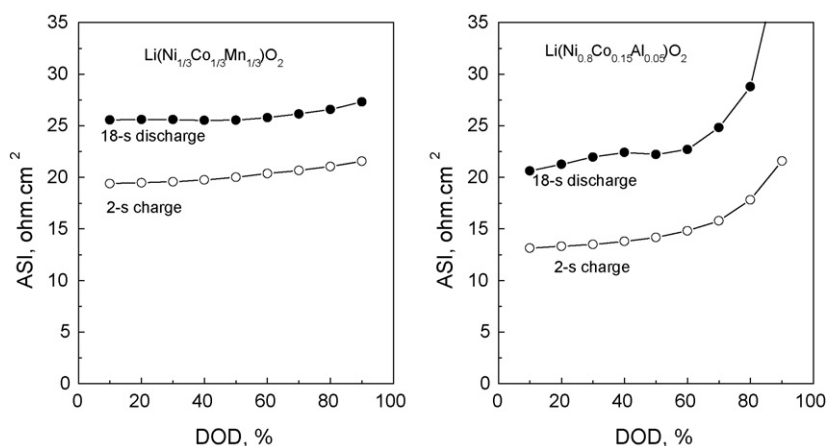


Fig. 2. Pulse power ASI as a function of DOD for a $\text{C}/\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{C}/\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ cell chemistries.

powders were washed with acetonitrile several times. The resulting materials were then dried at 80°C under vacuum for 24 h and thereafter were stored inside an argon-filled glove box. The inductively coupled plasma (ICP) analysis results revealed that after delithiation, $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ were obtained, respectively.

Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Siemens D5000 powder diffractometer using $\text{Cu K}\alpha$ radiation in the angular range of 10° – 80° (2θ) with a 0.02° (2θ) step. The structural parameters were calculated using Rietveld profile matching refinement of the XRD diagrams.

Thermal gravimetric analysis (TGA) experiments under a purified air flow were conducted on the chemically delithiated $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powders that were placed inside platinum pans, where the reference pan of the furnace consisted of an empty platinum pan. The data were collected using a Seiko Exstar 6000 instrument at a scan rate of 5°C min^{-1} in the temperature range of 25 – 600°C .

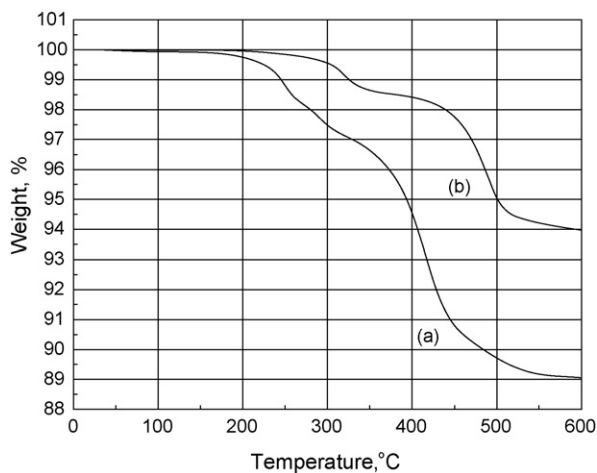


Fig. 3. Thermal gravimetric analysis (TGA), conducted under purified air atmosphere, of the (a) $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and (b) $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ delithiated cathodes.

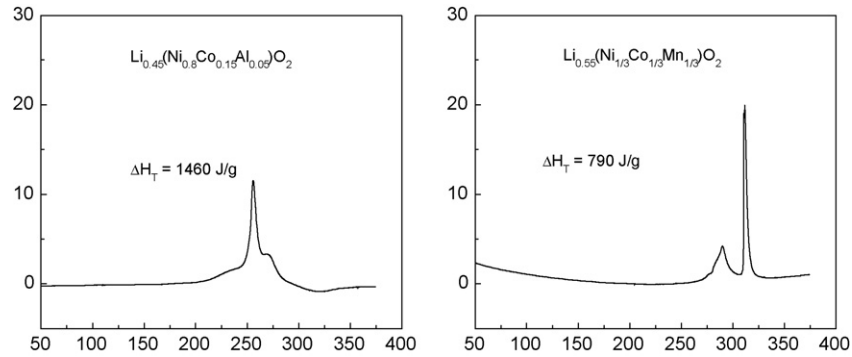


Fig. 4. DSC profiles of $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powders in the presence of 1.2 M $\text{LiPF}_6/\text{EC}/\text{EMC}$ (3:7 wt%) electrolyte.

Differential scanning calorimetry (DSC) experiments were conducted on the chemically delithiated powders using a Perkin-Elmer Pyris 1 instrument. Typically, 3 mg of $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ or $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powders and 3 μL of electrolyte were hermetically sealed inside stainless-steel high-pressure capsules to prevent leakage of the pressurized solvents. The DSC curves were recorded between room temperature and 375 °C at a scan rate of 10 °C min^{-1} . An empty stainless-steel capsule was used as a reference pan. To ensure reproducibility, at least two measurements were conducted for each data point.

Accelerated rate calorimetry (ARC) experiments were carried out on stainless-steel sealed tubes (2.7 g) containing 100 mg of $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ or $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ and 100 mg of a 1.2 M $\text{LiPF}_6/\text{EC}:\text{EMC}$ (3:7 wt%) electrolyte. The sealed tubes were mounted in the ARC calorimeter inside the containment vessel. The bombs were initially heated to 60 °C, kept for 5 min at this temperature, and then a 17-min exothermic reaction search was launched with a self-heating rate (SHR) greater than 0.02 °C min^{-1} . If no reaction activity

occurred, the temperature was programmed to increase by 10 °C at a rate of 5 °C min^{-1} and then a new wait-search cycle was carried out until the detection of an exothermic reaction or until the temperature reached 400 °C.

3. Results and discussion

Fig. 1 shows the XRD patterns of the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ pristine cathodes and their de-intercalated phases, $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$. In all cases, the observed diffraction lines can be indexed based on the R-3m space group and are consistent with the layered structure of $\alpha\text{-NaFeO}_2$.

The hexagonal lattice parameters for the respective materials are $a_h = 2.862 \text{ \AA}$, $c_h = 14.171 \text{ \AA}$ for $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$; and $a_h = 2.860 \text{ \AA}$, $c_h = 14.244 \text{ \AA}$ for $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$. We noticed that after delithiation, both phases generally maintained the layered structure of $\alpha\text{-NaFeO}_2$ in spite of the deintercalation of 55% of the initial lithium ions from between the metallic planes of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and

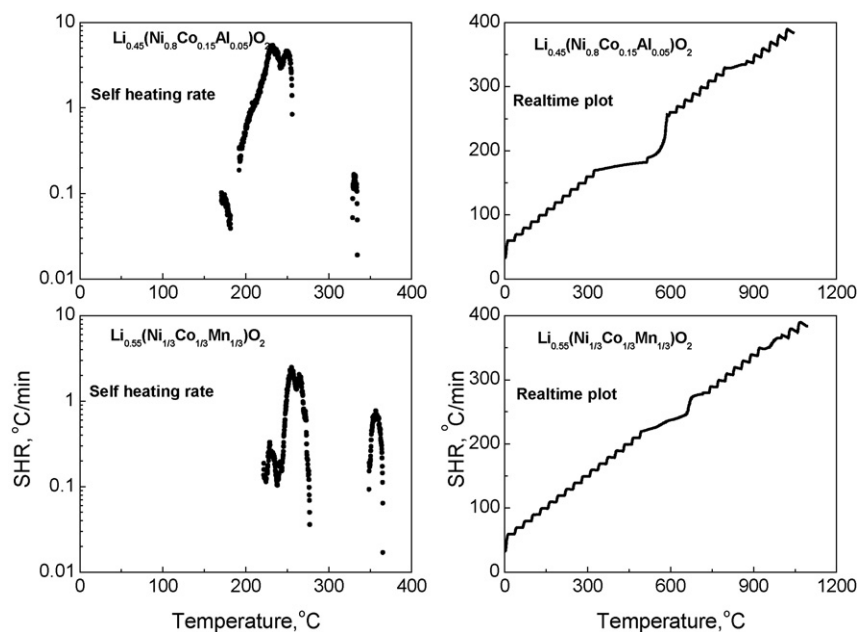


Fig. 5. ARC data (real-time and self-heating rate plots) of $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ in the presence of 1.2 M $\text{LiPF}_6/\text{EC}/\text{EMC}$ (3:7 wt%) electrolyte.

$\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$. The unit cell parameters were calculated using Rietveld profile matching refinement of the corresponding XRD diagrams (Fig. 1): $a_h = 2.830 \text{ \AA}$, $c_h = 14.432 \text{ \AA}$ for $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $a_h = 2.829 \text{ \AA}$, $c_h = 14.444 \text{ \AA}$ for $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$. In both cases, an expansion of the c parameter was observed compared with the initial phases.

The HPPC tests were carried out on graphite/ $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and graphite/ $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ cells using a 10 C pulse rate. Fig. 2 shows the area specific impedance (ASI) for the 18-s pulse discharge and 2-s regenerative charge as a function of depth of discharge (DOD). To meet the power requirement for HEVs, the ASI values should be lower than those calculated from the Argonne National Laboratory battery design spreadsheet model for a 25-kW battery pack, which are $35 \Omega \text{ cm}^2$ for an 18-s discharge and $25 \Omega \text{ cm}^2$ for a 2-s charge pulse. As can be seen in Fig. 2, both cell chemistries can meet and exceed the HPPC requirements for HEVs. In the case of the $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ electrode, the ASI values are steady over the total range of the depth of discharge, although they are slightly higher than those of the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ electrode.

Fig. 3 shows the thermal gravimetric analysis curves of $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ recorded between room temperature and 600°C under a purified air atmosphere. In both cases, the weight loss observed for these chemically delithiated oxides was associated with the oxygen release from their structures, as reported in previous reports [9,10]. However, their tendencies to release oxygen are different and strongly depend upon their structural stabilities.

Note that in situ gas analysis during the TGA experiment was conducted on both $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powders under a high-purity N_2 flow. The only gas, other than nitrogen, detected by mass spectrometry during the weight loss was oxygen, in agreement with the report of Guilnard et al. [9,10].

In the case of the thermodynamically less stable $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$, the loss at 600°C of 11 wt% oxygen was accompanied by significant structural damage, whereas the mechanism by which $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ lost oxygen was slowed down and resulted in the loss of 6 wt% oxygen only. More importantly, the results show that the oxygen release from $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ occurred starting from 250°C instead of 190°C as was observed in the case of $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$. These fundamental differences in the thermal degradation behavior of these materials indicate that the $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ has better safety characteristics than that of the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ material.

To initiate the study of their reactivity with electrolytes, DSC and ARC curves were first recorded on $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powders without electrolyte. In this case, no exothermic reactions were observed.

The reactivity of layered $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ cathode materials in the presence of 1.2 M $\text{LiPF}_6/\text{EC}/\text{EMC}$ (3:7 wt%) electrolyte was initially studied by the DSC technique (Fig. 4). The results of this study

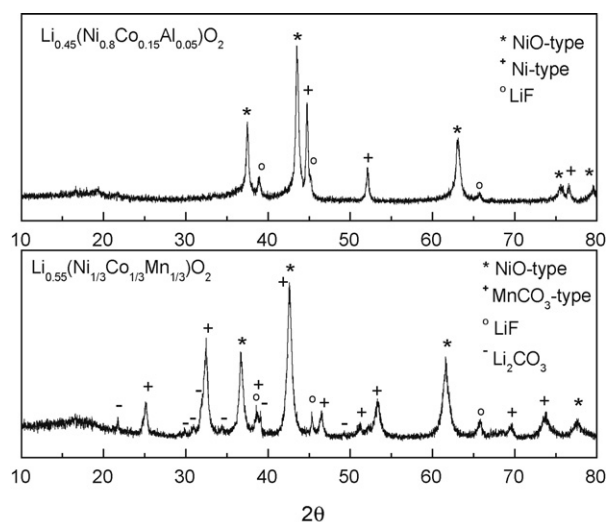


Fig. 6. XRD patterns recorded on the $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ samples recovered after the ARC experiments as described in Fig. 5.

show the following: (1) the onset reaction temperature (210°C) for the $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ compound was found to be lower than that (260°C) for the $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ compound; (2) the main exothermic reaction occurs around 250 and 300°C for the $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$, respectively and (3) the total generated heat for $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ was almost twice that measured in the case of $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$.

To corroborate these DSC observations, cathode/electrolyte reactivity was investigated by ARC. The study confirms in general the DSC results, and shows that the oxidation of the 1.2 $\text{LiPF}_6/\text{EC}/\text{EMC}$ (3:7 wt%) electrolyte occurs at a lower temperature (170°C) when mixed with $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ material versus 220°C for $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ material, with the generation of less heat in the case of the latter (Fig. 5). In the absence of the electrolyte, no exothermic reaction occurred as said above. Therefore, we believe that the heat measured by ARC or DSC is due to the oxidation of the electrolyte after reaction with the oxygen released from $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ materials at high temperature as reported by other researchers [11–14]. The initiation of the oxidation of the electrolyte itself depends on the structural stability of these delithiated cathodes. The lower the structural stability of cathodes, the higher their tendency of oxygen release. The combination of DSC and ARC clearly illustrates that the safety of Li-ion cells based on the $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ electrode material is expected to be much improved compared with the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ cells.

The XRD results reveal the presence of a NiO-type phase and LiF for both $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ and $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ after reaction with the electrolyte (Fig. 6). In addition, a Ni-metal-type phase was specifically found for the $\text{Li}_{0.45}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ material because of an O_2 release from a part of the resulting NiO-type phase. In the case of $\text{Li}_{0.55}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$, there is formation of two additional phases, MnCO_3 and Li_2CO_3 , that form after a reac-

tion with the CO₂ gas generated after the decomposition of the electrolyte.

4. Conclusions

This study details the safety characteristics of both Li(Ni_{0.8}Co_{0.15}Al_{0.05})O₂ and Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O₂ systems. From the standpoint of power characteristics, both the Li(Ni_{0.8}Co_{0.15}Al_{0.05})O₂ and Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O₂ cell chemistries meet and exceed the FreedomCAR requirement to power HEVs. However, it is clear from this safety study that the adoption of Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O₂ in Li-ion cells will significantly improve cell abuse tolerance and, thus, make this technology suitable for HEV applications.

Acknowledgements

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References

- [1] I. Bloom, B.W. Cole, J.J. Sohn, S.A. Jones, E.G. Polzin, V.S. Battaglia, G.L. Henriksen, *J. Power Sources* 101 (2001) 238.
- [2] C.H. Chen, J. Liu, M.E. Stoll, G. Henriksen, D.R. Vissers, K. Amine, *J. Power Sources* 128 (2004) 278.
- [3] I. Belharouak, D. Vissers, K. Amine, *J. Electrochem. Soc.* 153 (11) (2006) A2030.
- [4] E.P. Roth, D.H. Doughty, *J. Power Sources* 128 (2004) 308.
- [5] I. Belharouak, Y.-K. Sun, J. Liu, K. Amine, *J. Power Sources* 123 (2003) 247.
- [6] I. Belharouak, W. Lu, D. Vissers, K. Amine, *Electrochem. Commun.* 8 (2006) 329.
- [7] S. Venkatraman, A. manthiram, *Chem. Mater.* 14 (2002) 3907.
- [8] S. Venkatraman, Y. Shin, A. manthiram, *Electrochem. Solid-State Lett.* 6 (2003) A9.
- [9] M. Guilmard, L. Croguennec, D. Denux, C. Delmas, *Chem. Mater.* 15 (2003) 4476.
- [10] M. Guilmard, L. Croguennec, C. Delmas, *Chem. Mater.* 15 (2003) 4484.
- [11] D.D. MacNeil, T.D. Hatchard, J.R. Dahn, *J. Electrochem. Soc.* 148 (7) (2001) A663.
- [12] D.D. MacNeil, J.R. Dahn, *J. Electrochem. Soc.* 149 (7) (2002) A912.
- [13] H. Maleki, G. Deng, A. Anani, J. Howard, *J. Electrochem. Soc.* 146 (9) (1999) 3224.
- [14] H. Arai, M. Tsuda, K. Saito, M. Hayashi, Y. Sakurai, *J. Electrochem. Soc.* 149 (4) (2002) A401.