

## Investigation of hydrogen content in chemically delithiated lithium-ion battery cathodes using prompt gamma activation analysis

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Lithium-ion batteries are widely used as a power source for portable electronic devices. Currently, only 50–70% of the theoretical capacity of the layered oxide cathode (positive electrode) materials could be reversibly used. The reason for this limitation is not fully understood in the literature. Recent structural and chemical characterizations of chemically delithiated (charged) cathodes suggest that loss of oxygen from the lattice may play a role in this regard. However, during the chemical delithiation process any proton inserted from the solvent could adversely affect the oxygen content analysis data. The challenge in addressing this issue is to detect and determine precisely the proton content in the chemically delithiated samples. The prompt gamma-ray activation analysis (PGAA) facility at the Nuclear Engineering Teaching Laboratory (NETL) is used to determine the proton content in the layered oxide cathode  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  before and after chemical delithiation. The data are compared with those obtained with Fourier transform infrared (FTIR) spectroscopy, which can provide mainly qualitative analysis. The technique has proved to be promising for these compounds and will be applied to characterize several other chemically delithiated  $\text{Li}_{1-x}\text{Co}_{1-y}\text{M}_y\text{O}_2$  ( $\text{M} = \text{Cr, Mn, Fe, Ni, Cu, Mg, and Al}$ ) cathodes.

### Introduction

The exponential growth in portable electronic devices such as cellular phones and laptop computers has created an ever-increasing demand for compact, lightweight power sources offering high energy densities. In this regard, lithium-ion batteries have become appealing as they provide higher energy density compared to the other rechargeable systems such as lead-acid, nickel-cadmium, and nickel-metal hydride batteries as shown in Fig. 1.<sup>1</sup> The commercial lithium-ion cells currently use the layered  $\text{LiCoO}_2$  cathode as it offers a high discharge voltage of around 4 V and exhibits good electrochemical performance.<sup>2</sup> However, only 50% of the theoretical capacity of  $\text{LiCoO}_2$  could be utilized in commercial lithium-ion cells, which corresponds to a reversible extraction of 0.5 lithium per Co and a practical capacity of 140 mAh/g, limiting the energy density. More recently, the analogous layered  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  has been found to offer a capacity of 150–200 mAh/g depending on the synthesis conditions, which corresponds to 55–70% of the theoretical capacity.<sup>3,4</sup> Despite the same O3 structure, shown in Fig. 2, the layered oxides differ significantly in their practical capacities and energy densities, and the factors that cause the limitation are not fully understood in the literature.

Recent investigations by a chemical delithiation technique using a powerful oxidizer  $\text{NO}_2\text{BF}_4$  in acetonitrile medium suggest that the chemical instability resulting in the loss of oxygen from the lattice may play a crucial role in determining the reversible capacity limits of the layered  $\text{LiMO}_2$  cathodes.<sup>5–7</sup> The chemical

delithiation technique gives access to bulk  $\text{Li}_{1-x}\text{MO}_2$  samples free from carbon, binder, and electrolyte unlike the electrochemical delithiation. The bulk  $\text{Li}_{1-x}\text{MO}_2$  samples can be analyzed to determine accurately the lithium content, the oxidation state of  $\text{M}^{n+}$ , and the oxygen content.<sup>5–7</sup> However, there is a possibility that protons could be inserted into the cathode oxide lattice during the chemical delithiation process. If so, it could influence the oxygen content analysis data and the conclusions adversely. The challenge in addressing this issue is to detect and determine the proton (hydrogen) contents precisely in the chemically delithiated layered oxide cathodes.

Several researchers have shown the successful application of a reactor based prompt gamma-ray activation analysis (PGAA) for the detection of trace concentration of many light elements.<sup>8–11</sup> The primary goal of this investigation is to use the PGAA facility at the Nuclear Engineering Teaching Laboratory (NETL) of The University of Texas at Austin (UT-Austin) to determine accurately the hydrogen content, if any, in the chemically delithiated layered oxide samples. In order to check the feasibility of employing the PGAA technique for analyzing the proton content in the layered oxides, this paper focuses on analyzing the  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  system before and after extracting lithium in an aqueous medium by treating with dilute  $\text{H}_2\text{SO}_4$ . The PGAA results are complemented with the Fourier transform infrared (FTIR) spectroscopic data of the samples; FTIR spectroscopy generally provides qualitative information about the presence of lattice protons. Additionally, PGAA is also used to determine the changes occurring in lithium and manganese contents during the chemical

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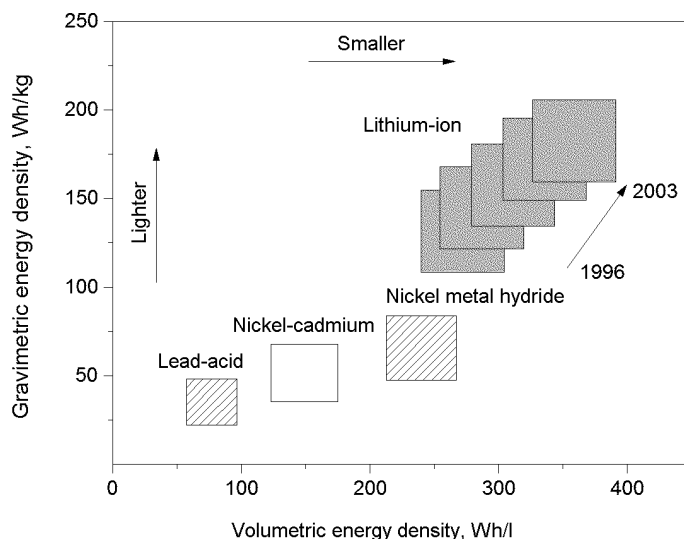


Fig. 1. Comparison of the volumetric and gravimetric energy densities of various rechargeable battery systems

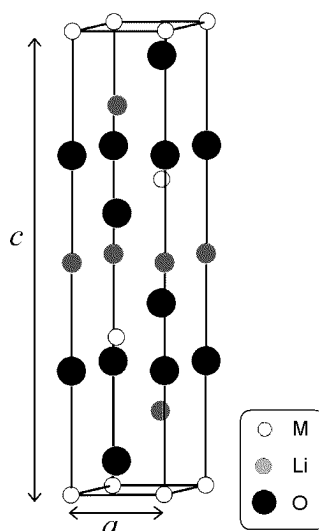


Fig. 2. Crystal structure of the ideal O3-type layered  $\text{LiMO}_2$

delithiation process. The sample preparation through delithiation, PGAA facility description, experimental procedure, the FTIR spectroscopic data and PGAA results of the samples are discussed.

## Experimental

### Chemical synthesis of layered oxides

The parent layered oxide sample  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  was synthesized by a co-precipitation procedure. Stoichiometric amounts of nickel(II) acetate (99+%, Alfa Aesar) and manganese(II) acetate (99+%, Acros Organics) were dissolved in de-ionized water and added drop by drop into a 0.1M KOH (laboratory grade,

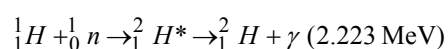
Fischer Scientific) solution to co-precipitate the metal ions as hydroxides. The co-precipitate was filtered, washed with de-ionized water, and dried overnight at 100 °C in an air oven. The co-precipitate of nickel and manganese was then ground with a required amount of  $\text{LiOH}\cdot\text{H}_2\text{O}$  (laboratory grade, Fischer Scientific) and fired first at 480 °C for 3 hours and then at 900 °C for 3 hours in air. Chemical lithium extraction was carried out by stirring the  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  powder with 2.5N  $\text{H}_2\text{SO}_4$  for 2 days, followed by filtering, washing, and drying at 100 °C. Lithium extraction with dilute acid involves a disproportionation reaction of  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$  (in solid) and  $\text{Mn}^{2+}$  (in solution).<sup>12</sup> While the parent  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  is expected to contain no proton, the delithiated  $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$  has the possibility of

containing some protons inserted during the chemical delithiation process. Chemical analysis for lithium content and the oxidation state analysis suggested a composition of  $\text{H}_{0.5}\text{Li}_{0.3}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$  for the delithiated sample assuming no oxygen is lost during the lithium extraction process. The samples for the PGAA analysis were prepared in an argon-filled glove box to avoid any contact of the samples with the ambient. FTIR spectra were recorded with pellets made with KBr and the sample.

### Challenges of proton detection

PGAA is a nondestructive nuclear analytical technique that can be used to obtain information on the isotopic constituents in a sample, in quantities ranging from trace levels to major abundances.<sup>13</sup> Other techniques such as FTIR spectroscopy, thermogravimetric analysis (TGA), and mass spectroscopic analysis have also been used for hydrogen detection. PGAA offers significant advantages compared to other techniques with respect to the measurement accuracy and detecting trace amounts of protons (hydrogen).<sup>13,14</sup>

Natural hydrogen is composed of H-1 (99.985%) and H-2 (0.015%). Hydrogen analysis using NAA is not possible as the principal radioactive activation product, H-3, is produced in minute quantities and it does not decay by gamma-ray emission, an essential characteristic for NAA.<sup>15</sup> Prompt gamma-ray spectra generally cover a wide range of energies and individual gamma-rays are well separated even for spectra with many prompt gamma-energies. Hydrogen has a single prompt gamma-peak (100% yield) at 2.223 MeV, and therefore, it is straightforward to detect with PGAA:



The efficiency of PGAA analysis relies on the strength of the prompt gamma-peak, background peaks, and interference peaks. A reactor based neutrons source can be used to enhance the prompt gamma-signal for light nuclides. The PGAA facility at NIST has been used to determine the hydrogen content in doped  $\text{SrCeO}_3$ <sup>16</sup> and titanium.<sup>17</sup> Researchers at NIST have applied PGAA to analyze the hydrogen uptake in HZSM-5 zeolites.<sup>18</sup> NIST uses PGAA analysis to certify many light elements including hydrogen and boron concentrations for standard reference materials (SRMs). Budapest facility has shown utility of PGAA analysis to determine hydrogen.<sup>19</sup> The PGAA facility at UT-Austin is being used to detect and analyze hydrogen, for the first time, in layered oxides of interest to lithium-ion batteries. Characterization of the detector facility and hydrogen detection limit are presented elsewhere.<sup>20,21</sup> The first task of this work was to demonstrate the

capability to analyze samples with a wide range of hydrogen and other light elements using the NETL PGAA facility at UT-Austin.

### Prompt gamma activation analysis (PGAA)

*NETL PGAA facility:* The guided beam delivers a thermal equivalent neutron flux of  $(1.5 \pm 0.6) \cdot 10^7 \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$  to the focal plane with no cold moderation, and  $(4.6 \pm 0.7) \cdot 10^7 \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$  while the cold moderator is frozen to 26 K.<sup>22</sup> Data from the HPGe detector is acquired using a Canberra DSA digital spectroscopy system that has a 16k channel MCA. The Canberra Genie 2000 v1.4 Gamma Acquisition software is used for sample acquisition and analysis. The energy and efficiency calibration of the detector is done in accordance with the standard procedures used for such systems. The resolution of the detector at the 2.2223 MeV is 2 keV. Cryogenic refrigerator and the vacuum pump system related to the cold source are under modifications currently. For all the experiments detailed in this work, thermal neutron beam guide was used.

### Experimental procedure

All samples were handled in an inert argon environment and were pre-heated at 105 °C before they were put in the beam line for analysis. Special Teflon™ sample holders were used to minimize the presence of carbon, hydrogen, and any other low *Z* material that are typically present in polyethylene sample vials. The sample location was fixed using neutron radiography imaging. A helium based neutron counter was used to collect real time neutron fluence impinging the sample. The neutron fluence recorded for each experiment was then used for net count normalization. To maintain uniformity all sample including standards were irradiated at the same geometrical location and environmental condition. The concentration of hydrogen in all samples was determined by the comparative method. NIST standard reference material (SRM) 1632c (Coal) was used as the standard.

### Results and discussion

Three sets of experiments were performed. The first set of experiments was to verify the accuracy of proton detection in NIST SRM standard at the NETL PGAA. The second set of experiments was to determine hydrogen content (comparative method) in laboratory grade inorganic material  $\text{Ni}(\text{OH})_2$  (theoretically known hydrogen concentration) by using NIST SRM 1632c as a standard. The third set of experiments was carried out with the layered oxide sample  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  before

and after extracting lithium with dilute  $\text{H}_2\text{SO}_4$ . FTIR spectroscopy was performed on the  $\text{Ni}(\text{OH})_2$  and the layered oxides to verify qualitatively the presence of protons.

To test the feasibility and applicability of the NETL PGAA system to determine the presence of protons with high accuracy, system verification experiments were performed. In order to perform this test, the NIST SRM 1632c standard was selected. The certified hydrogen concentration in NIST SRM 1632c is  $51100 \pm 1200 \mu\text{g/g}$ .<sup>23</sup> Laboratory grade sucrose sample was suggested as the second compound to check the reported concentration of NIST SRM 1632c.<sup>24</sup> The hydrogen concentration determined from the theoretical calculations of sucrose is  $64779 \pm 1300 \mu\text{g/g}$ . Both the samples were irradiated for 4 hours at 500 kW. The spectra for sucrose, SRM 1632c, and background are shown in Fig. 3. The NETL measured value for NIST SRM 1632c is within 1% of the reported certificate values (Table 1).

Two background spectra (with just the empty sample vial) at separate times were collected to characterize the background hydrogen content. There is observable concentration of hydrogen in the background. The background correction is made by subtracting the

hydrogen count rate of the background spectra from the sample spectra. The major contribution of hydrogen in the background is believed to be from moisture content in the environmental air. The hydrogen background is very low as compared to the hydrogen signal from both the NIST SRM 1632c and sucrose and hence the contribution of statistical error is negligible. The hydrogen concentration in some of the layered oxide samples is expected to be very low ( $<100 \mu\text{g/g}$ ). The statistical error from the background subtraction is expected to dominate the total error contribution for the samples with low concentration hydrogen.

To reduce the hydrogen background, a Teflon™ bag filled with helium was put around the sample. This procedure reduced the hydrogen background by ~5% although it is not reduced enough to the levels desired for future planned experiments. Further improvements are being explored.

Laboratory grade  $\text{Ni}(\text{OH})_2$  sample was irradiated for 4 hours at 500 kW and the proton concentration was determined using the comparative method. NIST SRM 1632c was used as the standard. The measured concentration of hydrogen in  $\text{Ni}(\text{OH})_2$  from PGAA is  $19660 \pm 490 \mu\text{g/g}$ , which compares well to the theoretical value of  $21744 \pm 2821 \mu\text{g/g}$ .

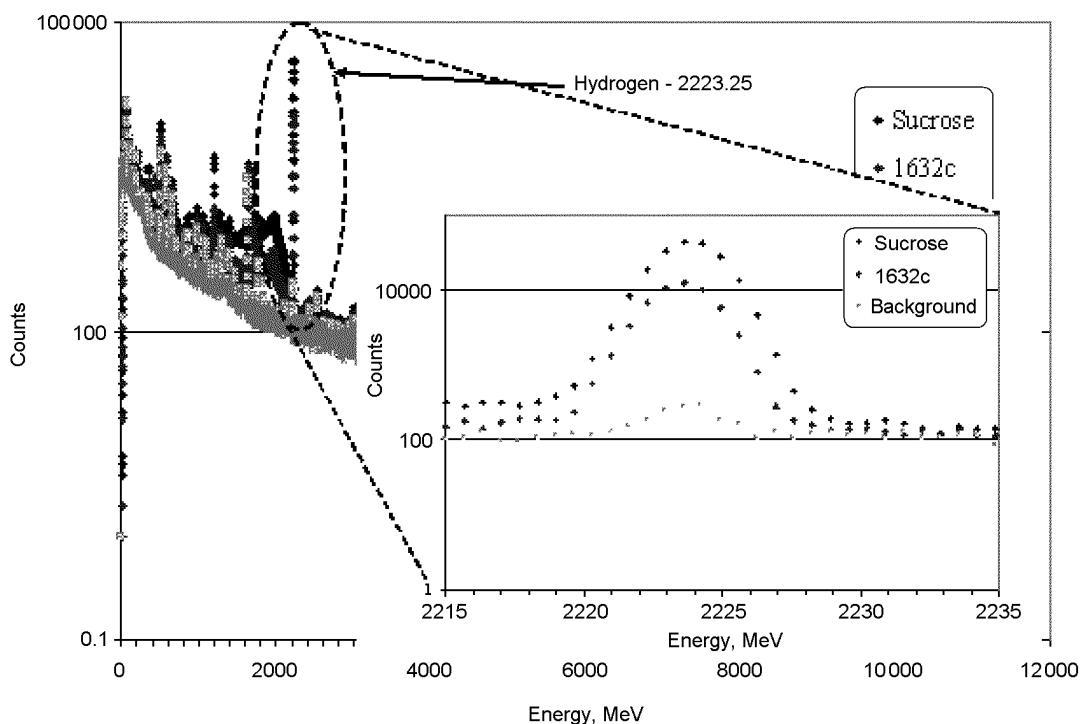


Fig. 3. PGAA spectrum with an inset of the hydrogen peaks for sucrose, NIST SRM 1632c and background

Table 1. Calculated certified concentration of hydrogen in NIST SRM 1632c and sucrose

Sample	Standard	Concentration, $\mu\text{g/g}$	Certified value, $\mu\text{g/g}$	Difference, %
NIST SRM 1632c	Sucrose	$50689.01 \pm 1048.94$	$51100.00 \pm 1200.00$	0.80
Sucrose	NIST SRM 1632c	$65304.23 \pm 1217.55$	$64779.00 \pm 1300.00$	0.81

Two different samples of the layered oxides were considered for this study:  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  before chemical lithium extraction (parent), and after chemical lithium extraction (delithiated daughter). The relative changes in the primary constituents (lithium, manganese, and hydrogen) of the compounds were analyzed. Figures 4 and 5 show the gamma-spectrum peaks for Mn – 314.4, Li – 2032.5 keV and Mn – 2044.7, respectively. While there are no observable Li and Mn peaks in the background spectrum, there are distinct peaks in the spectra of the parent and delithiated samples.

The hydrogen peak in the background spectra is comparable to that in the parent compound. For the delithiated daughter sample, the hydrogen count is much higher compared to the background (Fig. 6). The difference in peak counts between the parent compound

and the background is low  $104 \pm 81$ , and is close to the statistical error. Figure 7 shows the net count after the background subtraction. The reduction in hydrogen background is desired for future experiments to lower the uncertainty and improve the statistical error. Figure 8, shows the fluorine peak (1633.1 keV, delayed 11 s) for the background and the two layered oxide samples. The Compton continuum is observed to be much lower in background as compared to the samples, although the overall fluorine counts are comparable. The ratio of the fluorine peaks between samples and background spectra is used as an additional normalization factor to address any systematic variation. The fluorine background comes from the Teflon™ the material that makes up the sample holder, hence, it can be used as an additional constant background peak check. Fluorine is absent in the material under investigation and hence is exclusively from the sample holder.

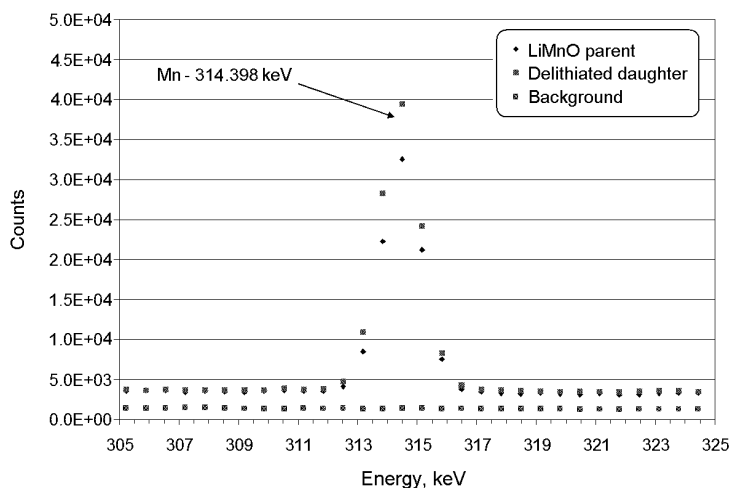


Fig. 4. Mn-314.14 keV peaks shown for the two samples and background

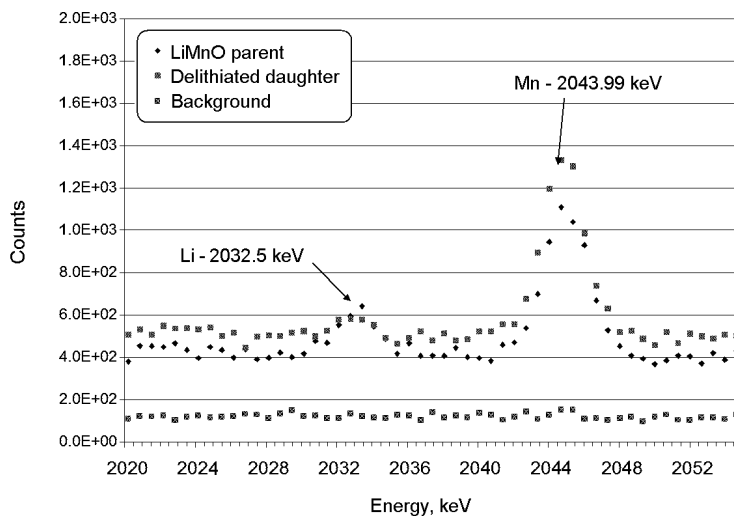


Fig. 5. Li-2032.5 keV and Mn-2043.99 keV peaks shown for the two samples and background

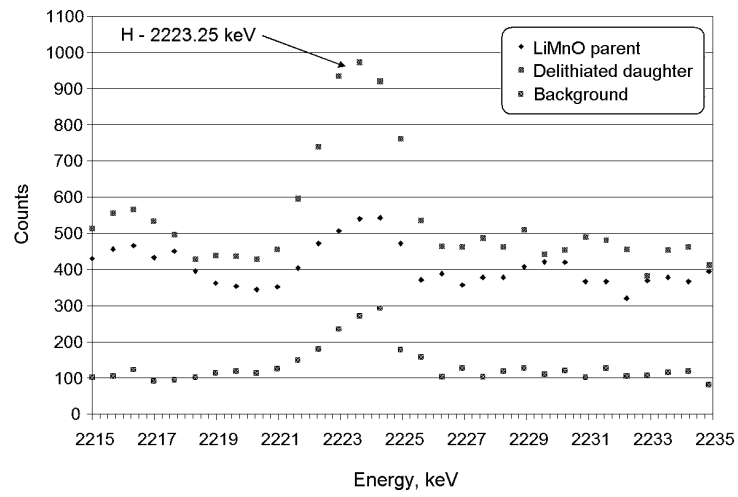


Fig. 6. H-2223.25 keV peaks shown for the two samples and background

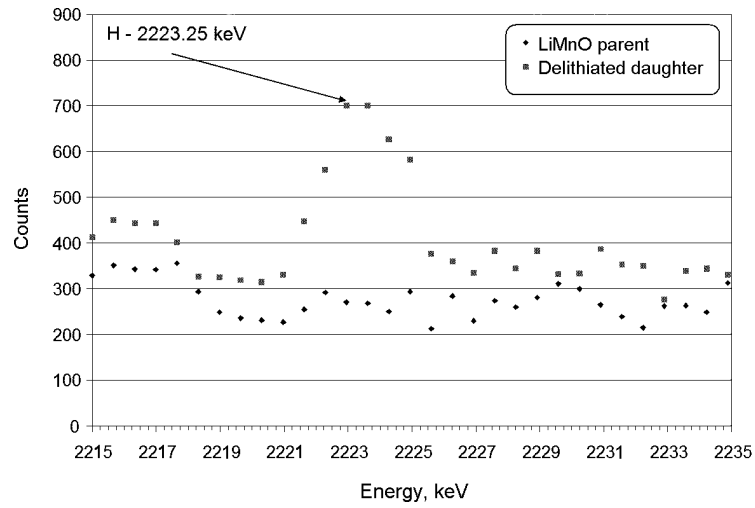


Fig. 7. Background subtracted H-2223.25 keV peaks shown for the two samples

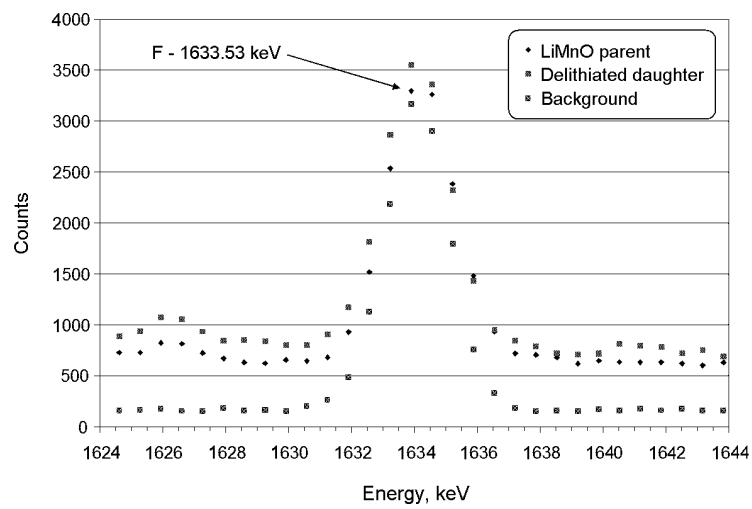


Fig. 8. F-1633.53 keV peaks shown for the two samples and background

Net counts under individual peaks of Li, Mn and H were evaluated from the gamma-spectra. The counts are normalized with the total neutron fluence (collected during spectrum acquisition), sample weight, and the fluorine peak ratio (sample spectrum to background spectrum). Through this normalization we are able to reduce any systematic and acquisition variation in net peak counts obtained from PGAA. Table 2 lists the normalized counts obtained from PGAA analysis.

The counts for Li in the delithiated daughter are reduced as compared to that in the parent sample, which is expected since Li is removed from the parent sample during the process of delithiation. Note the relative Mn counts are observed to increase in the delithiated daughter because the counts are normalized to weight and since Li is removed during the delithiation process, the net concentration of Mn is increased. The hydrogen counts are observed to increase, which shows the insertion of proton (hydrogen) into the delithiated daughter compound during the delithiation process. The insertion of proton is understandable considering the aqueous sulfuric acid medium used for the delithiation

process. The net concentration of hydrogen concentration determined in the delithiated daughter is  $2399 \pm 108 \mu\text{g/g}$ . The expected value of proton based on the analyses of lithium content and the oxidation state of manganese in the delithiated daughter is  $5000 \mu\text{g/g}$ , assuming no oxygen is lost from the lattice during the delithiation process and the oxygen content remains as 2.00 as in the parent compound. The lower experimental value of proton content obtained from the PGAA suggests that an oxygen loss could indeed be occurring during the delithiation process in the aqueous medium. Assuming an oxygen loss from the lattice occurs during the aqueous delithiation process, the chemical composition calculated from the proton content value obtained from the PGAA data is  $\text{H}_{0.22}\text{Li}_{0.3}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_{1.86}$ . To address this issue appropriate analysis of change in oxygen concentration is currently being investigated. Once the oxygen concentration is determined accurately appropriate confirmation on the oxidation states in manganese ( $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$ ) will be evaluated.

Table 2. Normalized gamma-counts for different elements

Element and its peak energy	Parent (normalized counts)	Delithiated daughter (normalized counts)
H-2223.3 keV*	3.37E-05	5.12E-04
F-1633.5 keV	3.56E-03	3.58E-03
Li-2032.5 keV	4.79E-04	1.69E-04
Mn-314.4 keV	4.76E-02	6.52E-02
Mn-2043.99 keV	2.11E-03	2.67E-03
Ratio 1 Li/Mn (2032.5/314.4 keV)	1.01E-02	2.58E-03
Ratio 2 Li/Mn (2032.5/2044.7 keV)	2.27E-01	6.32E-02

Counts are background subtracted.

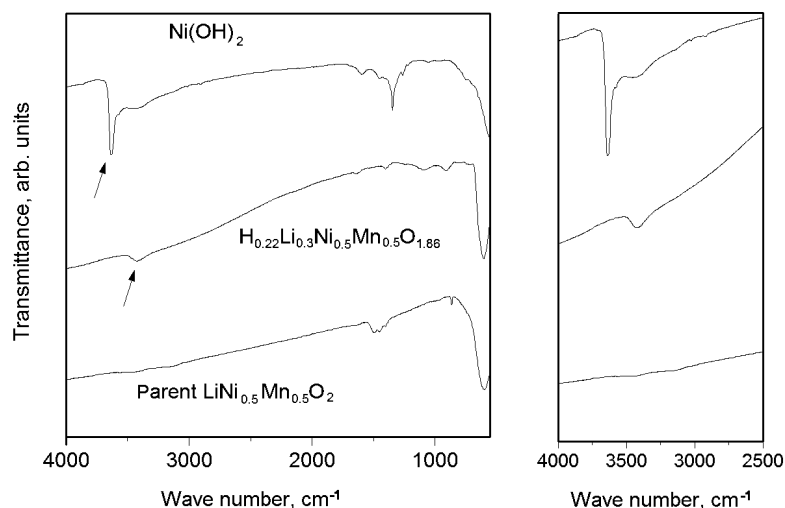


Fig. 9. Comparison of the FTIR spectra of  $\text{Ni}(\text{OH})_2$ , aqueous delithiated  $\text{H}_{0.22}\text{Li}_{0.3}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_{1.86}$ , and the parent  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ . Arrows indicate the position of the characteristic absorption band ( $\sim 3500 \text{ cm}^{-1}$ ) corresponding to O-H groups

*FTIR spectroscopy*

Figure 9 compares the FTIR spectra of Ni(OH)<sub>2</sub>, chemically delithiated H<sub>0.22</sub>Li<sub>0.3</sub>Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>1.86</sub> and the parent LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>. While both Ni(OH)<sub>2</sub> and the chemically delithiated H<sub>0.22</sub>Li<sub>0.3</sub>Ni<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>1.86</sub> samples show characteristic absorption band (~3500 cm<sup>-1</sup>) corresponding to O–H groups, the parent LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> does not show any absorption bands corresponding to O–H groups. These results are consistent with the proton data obtained from PGAA analysis.

**Conclusions and future work**

The verification experiments performed using sucrose and NIST SRM 1632c have shown that the NETL PGAA facility can be used with good accuracy for the determination of hydrogen concentration. Using the PGAA, we were able to observe the relative changes in the constituents of the layered LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> during the chemical delithiation process. The experiments show the absence of hydrogen in the parent LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> sample before delithiation as expected and small amounts of hydrogen in the chemically delithiated samples synthesized in an aqueous acid medium. The PGAA data gives an accurate quantitative determination of the proton content compared to the qualitative or semi-quantitative information generally obtained from the traditionally used techniques like FTIR or TGA.

The systematic errors, like differential scattering, self-absorption, and sample geometries do not seem to be major contributors since the error in the measured value of the NIST SRM 1632c is less than 1%. The statistical error from background subtraction in these measurements dominates the total error. The high background can become an issue when the proton content is extremely low. Improvement in the detection limits of hydrogen and reduction in the statistical error in determining low concentrations of protons are currently being pursued through better background suppression techniques.

However, the data presented here refer to samples synthesized in aqueous medium, which is prone to incorporate proton into the sample lattice. Recognizing that the PGAA could indeed be used to detect proton quantitatively in layered oxide materials (of interest to lithium-ion batteries), our future experiments would focus on assessing whether any proton is inserted into the layered oxide lattice during the chemical delithiation process with NO<sub>2</sub>BF<sub>4</sub> in the nonaqueous acetonitrile medium. For example, the technique will be applied to characterize several Li<sub>1-x</sub>Co<sub>1-y</sub>M<sub>y</sub>O<sub>2</sub> (M=Cr, Mn, Fe, Ni, Cu, Mg, and Al, and 0 ≤ x ≤ 1) cathode materials obtained by chemically extracting lithium with NO<sub>2</sub>BF<sub>4</sub>

in acetonitrile medium. Such experiments will help to identify the factors that limit the practical capacities of the layered oxide cathodes of lithium-ion batteries and develop new cathode materials offering high reversible capacity and good long-term cyclability (rechargeability). Future work will also include the analysis of LiCoO<sub>2</sub> compound, which is the cathode material used currently in commercial lithium-ion battery. Determination of hydrogen in presence of <sup>60</sup>Co poses a unique challenge since the two peaks are less than 2 keV apart.

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**References**

1. Lithium Battery Energy Storage (LIBES) Publication, Technological Research Association, Tokyo, 1994.
2. K. MIZUSHIMA, P. C. JONES, P. J. WISEMAN, J. B. GOODENOUGH, *Mater. Res. Bull.*, 15 (1980) 783.
3. T. OHZUKU, Y. MAKIMURA, *Chem. Lett.*, (2001) 744.
4. Z. LU, D. D. MACNEIL, J. R. DAHN, *Electrochem. Solid State Lett.*, 4 (2001) A191.
5. R. V. CHEBIAM, F. PRADO, A. MANTHIRAM, *Chem. Mater.*, 13 (2001) 2951.
6. S. VENKATRAMAN, Y. SHIN, A. MANTHIRAM, *Electrochem. Solid State Lett.*, 6 (2003) A9.
7. S. VENKATRAMAN, A. MANTHIRAM, *Chem. Mater.*, 15 (2003) 3907.
8. R. M. LINDSTROM, R. L. PAUL, D. H. VINCENT, R. R. GREENBERG, *J. Radioanal. Nucl. Chem.*, 180 (1994) 271.
9. R. L. PAUL, R. M. LINDSTROM, A. E. HEALD, *J. Radioanal. Nucl. Chem.*, 63 (1997) 215.
10. T. BELGYA, Z. RÉVAY, B. FAZEKAS, I. HÉJJA, L. DABOLCZI, G. L. MOLNÁR, Z. KIS, J. ÖSTÖR, G. KASZÁS, *Proc. 9th Intern. Symp. on Capture Gamma-ray Spectroscopy and Related Topics*, Budapest, Hungary, 1996, p. 826.
11. G. MOLNÁR, Z. RÉVAY, T. BELGYA, *J. Radioanal. Nucl. Chem.*, 215 (1997) 111.
12. J. C. HUNTER, *J. Solid State Chem.*, 39 (1981) 142.
13. R. L. PAUL, R. M. LINDSTROM, *J. Radioanal. Nucl. Chem.*, 181 (2000) 243.
14. R. L. PAUL, *Amer. Lab.*, 15 (2002).
15. R. L. PAUL, *Analyst*, 122 (1997) 35R.
16. F. KRUG, T. SCHOBER, R. PAUL, T. SPRINGER, *Solid State Ionics*, 77 (1995) 185.
17. R. L. PAUL, H. M. PRIVETT, R. M. LINDSTROM, W. J. RICHARDS, R. R. GREENBERG, *Met. Mater. Trans.*, 27A (1996) 3682.
18. C. Y. JONES, B. H. TOBY, *Trans., Am. Nucl. Soc.*, 87 (2002) 482.
19. K. TOMPA, P. BÁNKI, M. BOKOR, G. LASANDA, L. VASÁROS, *J. Alloys Comp.* (in press).
20. S. K. AGHARA, S. VENKATRAMAN, A. MANTHIRAM, *ANS Annual Meeting*, Pittsburg, PA, June 13–17, 2004.
21. S. R. BIEGALSKI, S. K. AGHARA, E. ALVAREZ, T. C. GREEN, *227th ACS National Meeting*, Anaheim, CA, 2004.
22. B. W. WEHRING, K. UNLU, C. RIOS-MARTINEZ, *Appl. Radiation Isotopes*, 48 (1997) 1343.
23. National Institute of Standards and Technology, Certificate of Analysis, Standard Reference Material 1632c Bituminous, 2001.
24. Personal communication with S. LANDSBERGER and R. M. LINDSTROM.