Molten Salt Flux Synthesis to Reduce Cation Disorder in $Li_2MnO_3/LiMO_2$ (*M* = Mn, Ni, Co) Cathodes for Lithium Ion Batteries

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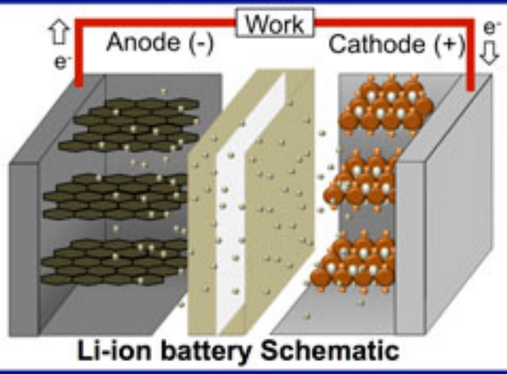
Abstract

Lithium ion batteries using Li_2MnO_3–$LiMO_2$ (*M* = Mn, Co, Ni) as the cathode had been extensively studied. Under 0 °C, batteries with this composite oxide present efficiency issues. This can be explained by a diffusion process with the lithium as consequences of the poor layer organization. LiCl salts can help improve this organization by resupplying the intercalated lithium to a molten mixture. Sensitivity studies directed to understand the effects of LiCl on the cathode material controlling variables as the synthesis time, and LiCl concentration will be accomplished. Electrochemical experiments using galvanostatic charge/discharge processes at C/5 and C/10 and impedances at different temperatures provide direct information of the diffusion and the dynamics of the batteries prepared with Li_2MnO_3 $LiMO_2$. Tap density analysis will be completed to have a better understanding of the behavior of the cathode after being packed in the batteries and an $AlPO_4$ coating. Results show an improvement in the capacity of the cathode after the LiCl flux.

Introduction

Batteries have proven to be a useful and convenient tool to store electrical energy in most electronic portable devices. Li-ion batteries have high specific energy compared to the solid lithium based ones and have less risk to react abruptly. Such secondary batteries use an intercalation process to store chemical energy in the anode that produces energy during the discharge process were Li-ions migrate to the cathode. There is a irreversible loss of capacity across the charging process in some of these batteries at the cathode side after the first cycle that is associated to oxygen displacement. A thin coating of $AlPO_4$ reduces this loss. Another factor that affects the capacity of the lithium ion batteries is the temperature. This could be associated to diffusion or mass transfer problems of the Li^+. To overcome such challenges, a LiCl molten flux has been employed. Will this LiCl flux process be successful in improving the capacity of the battery? A sensitivity study changing synthesis conditions had been performed to identify how both properties can help to increase battery capacity. **$LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$**, commercially available, and the synthetized Li_2MnO_3 have been used to produce the material for the cathode. Metallic lithium is used as the anode to complete a half cell.



Li-ion battery Schematic

Relevance to NASA

- **To produce advanced secondary Li-ion batteries with high capacity which are capable of working at temperatures under -20 °C.**
- **Such batteries provide a real alternative for future exploration missions to Europa and Titan, satellites of Jupiter and Saturn respectively.**

Research Questions

- **Will the LiCl molten flux to the cathode material improve the battery?**
- **Is the ceramic coating affecting the tap density?**

Project Methods

Li_2MnO_3 Synthesis:

Cathode Powder Synthesis:

Results

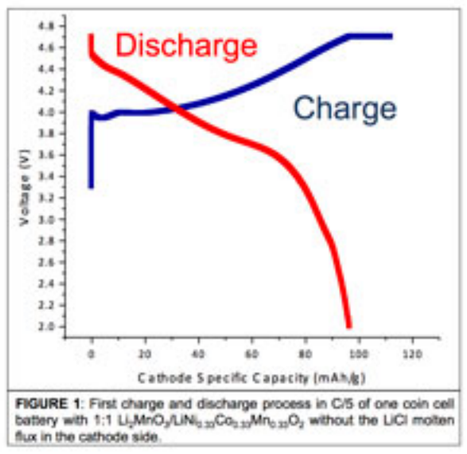


FIGURE 1: First charge and discharge process in C/5 of one coin cell battery with 1:1 $Li_2MnO_3/LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ without the LiCl molten flux in the cathode side.

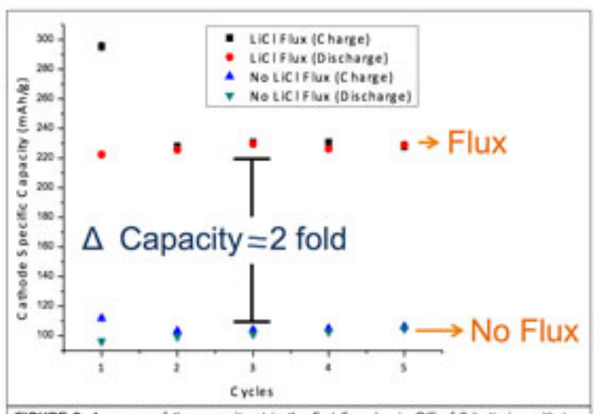


FIGURE 2: Averages of the capacity at in the first 5 cycles in C/5 of 8 batteries with two different conditions: average of 4 runs with LiCl flux, without the LiCl flux.

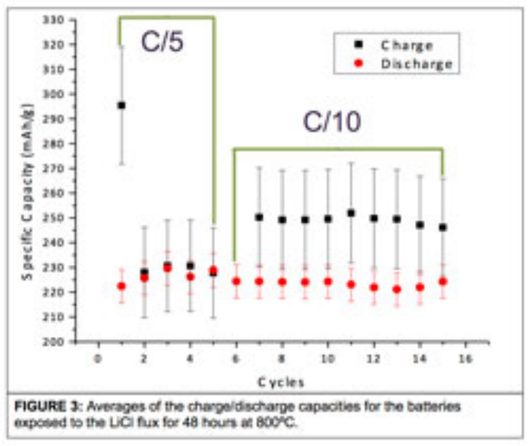


FIGURE 3: Averages of the charge/discharge capacities for the batteries exposed to the LiCl flux for 48 hours at 800ºC.

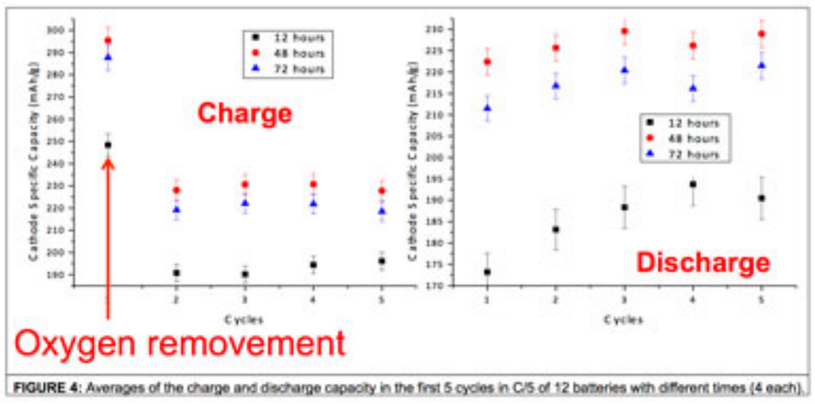


FIGURE 4: Averages of the charge and discharge capacity in the first 5 cycles in C/5 of 12 batteries with different times (4 each).

Conditions	Tap Density (g/mL)	
	$AlPO_4$ Coating	
	Before	After
$LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ Quallion	2.4	Starting Materials
Li_2MnO_3	1.4	
No LiCl Flux	1.6	1.3
48 hours, 800 °C	1.9	1.4

TABLE 1: Tap density results

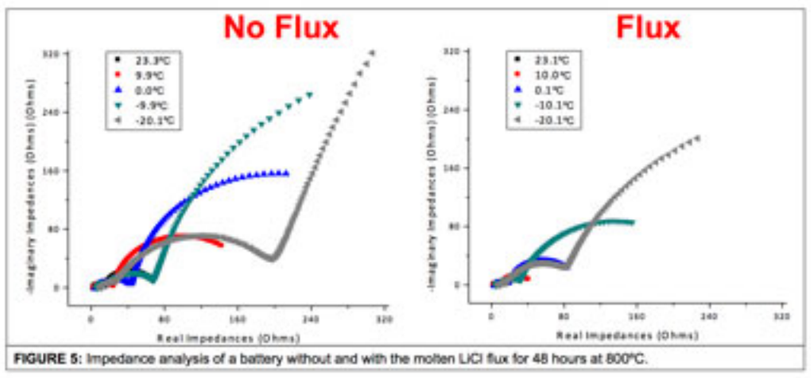


FIGURE 5: Impedance analysis of a battery without and with the molten LiCl flux for 48 hours at 800ºC.

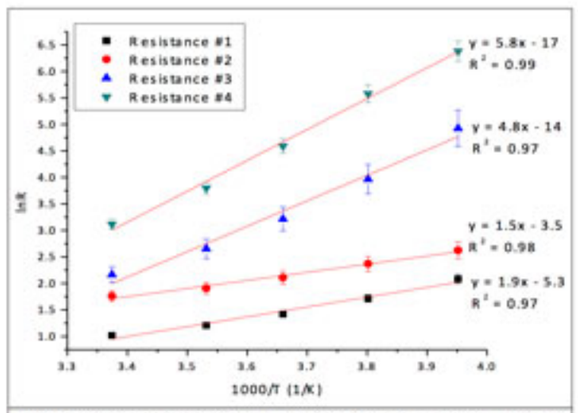


FIGURE 6: Impedance analysis at 5 different temperatures (from 23 ºC from the left to -20 ºC to the right) of the change in the resistances of an average of 4 batteries with the LiCl flux for 48 hours at 800 ºC.

Discussion

FIGURE 1 shows the galvanostatic charge and discharge at C/5 for the first cycle capacity around 100 mAh/g of the $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ / Li_2MnO_3 with the $AlPO_4$ coating and without the LiCl. **FIGURE 2** compares 8 batteries: 4 with the LiCl molten flux and 4 without. After the flux of the LiCl, there is an increase of more that the double the capacity. This behavior continues after the first 5 cycles in C/5. C/10 analysis was performed to assure the cycleability of the battery after the LiCl treatment. This property is still present after 15 cycles, as evidenced in **FIGURE 3**. The sensitivity analysis presented in **FIGURE 4** describes how the time exposed to the flux is crucial to the capacity of the battery. In 12 and 72 hours the capacity was reduced. The highest capacity was achieved in 48 hours. This can be related to the crystal organization of the particles and the particle sizes. Further X-ray Diffraction (XRD) and Scanning Electron Microscopy with Electron Dispersion Spectroscopy (SEM-EDS) analysis are needed to elucidate more details about both properties. Tap density results in **TABLE 1** present a pattern of how this property decreases after applying a ceramic coating. In the Electrochemistry Impedance Spectroscopy (EIS) analysis (**FIGURE 5**) the resistances decrease after the flux. This pattern continues even after decreasing the temperature down to -20 ºC. These results confirm the improvements of capacity after the LiCl molten flux at low temperatures. A fitting using ZSimpWin 3.30 software with a R(QR)(QR)(CR) circuit was completed. The calibration curves shown in **FIGURE 6** were produced after this fitting to observe the behavior of the real resistances. A linear correlation was obtained that relates the temperature and the resistances in the battery.

Conclusions

- LiCl molten flux proved to be a efficient synthesis method capable of increasing the capacity of $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ / Li_2MnO_3 by more than twice the initial capacity.
- Tap density decreases after the $AlPO_4$ coating.
- The time exposed to the flux is an important factor for the capacity reached after the synthesis.
- Resistances in the battery are reduced after the LiCl treatment.
- Li-ion battery capacity can be improved after the flux, providing a synthetic tool for NASA in cathode materials.

Future Works

- Characterization using XRD and SEM-EDS is needed to determine which physical factors can be related to this capacity change.
- XRD can provide evidence of the crystal structure changes, and the SEM technique will be useful to observe physical evidence of changes in the particle size.
- The EDS helps identify the distribution of the atoms across the surface providing additional chemical information of the system.
- Further electrochemical galvanostatic in C/10 and impedance spectroscopy analysis are needed to understand the behavior of these systems after the LiCl flux.

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