Addressing the Voltage Fade Issue with Li-Mn Rich Oxide Cathode Materials

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Overview

Timeline
- Start date: FY12
- End date: FY14
- Percent complete: 10%

Budget
- Total project funding: 100% DOE
- Funding in FY12: $2.5M

Barriers
- Development of a safe cost effective PHEV battery with a 40 mile all electric range that meets or exceeds all performance goals
  - Interpreting and mitigating complex electrochemical – structural relationships

Partners
- Collaborators: Ali Abouimrane, Daniel Abraham, Khalil Amine, Mahalingam Balasubramanian, Javier Baren Garcia-Ontiveros, Ilias Belharouak, Roy Benedek, Ira Bloom, Zonghai Chen, Dennis Dees, Kevin Gallagher, Hakim Iddir, Brian Ingram, Christopher Johnson, Wenquan Lu, Nenad Markovic, Dean Miller, Yan Qin, Yang Ren, Michael Thackeray, Lynn Trahey, and John Vaughey all from Argonne National Laboratory
Objectives

- Enable high energy composite lithium and manganese rich NMC (LMR-NMR) cathode materials, $x\text{Li}_2\text{MnO}_3.(1-x)\text{LiMO}_2$ (M = Ni, Mn, Co), for 40 mile PHEV applications.

- Focus on stabilizing open circuit voltage discharge profile during aging (i.e. voltage fade phenomenon) without sacrificing power, life, capacity and abuse tolerance.

Milestones FY12

- Definition of voltage fade established
- Test protocols established
- Benchmark materials properties using different synthesis techniques.
- Initiate detailed structural analyses of composite electrode structures at the Advanced Photon Source (APS) by X-ray diffraction, X-ray absorption and pair-distribution-function (pdf) analyses.
- Measure entropy changes measurement in standard composite cathode material.
Background: LMR-NMC

LMR-NMC, 4.6-2.0 V, 15 mA/g, RT

0.5Li₂MnO₃•0.5LiMn₀.₃₁Co₀.₂₅Ni₀.₄₄O₂

Good capacity retention, but...
Voltage Profiles shape changes

LMR-NMC, 4.6-2.0 V, 16 mA/g, RT

\(0.5\text{Li}_2\text{MnO}_3\cdot0.5\text{LiMn}_{0.31}\text{Co}_{0.25}\text{Ni}_{0.44}\text{O}_2\)

- This is not just energy density issue, but also battery management issue.

Down select and re-scope of significant portion of ANL work to solve voltage fade
The Approach

- A team that will share data and expertise to “fix” voltage fade in the LMR-NMC cathode materials. This will be a single team effort – not multiple PI’s working independently on the same problem.

- Definition of the problem and limitations of the composite cathode materials.
- Data collection and review of compositional variety available using combinatorial methods.
- Modeling and Theory.
- Fundamental characterization of the composite cathode materials.
- Understand the connections between electrochemistry and structure.
- Synthesis.
- Post treatment/system level fixes.

Moved effort from other projects to create the voltage fade team.
The Team

**Synthesis**
- Abouimrane, A
- Amine, K
- Belharouak, I
- Johnson, C
- Thackeray, M

**Theory**
- Benedek, R
- Iddir, H

**Characterization**
- Balasubramanian, M
- Ingram, B
- Chen, Z
- Miller, D
- Ren, Y
- Vaughey, J

**Diagnostics and Modeling**
- Abraham, D
- Dees, D.
- Gallagher, K
- Lu, W
- Barenco, H
- Markovic, N
- Trahey, L
Definition of the problem and limitations of the composite cathode materials.

- What is voltage fade and how do we quantify it?
- What does success look like?
- What are the parameters we have to work with?
- Working with OEM’s and other end-users to define “targets”
- What are the best test protocols to examine the problems?
Approach

Data collection and review of compositional variety available using combinatorial methods.

- Establish database.
- Survey the compositional phase space of the $x\text{Li}_2\text{MnO}_3 \cdot (1-x0.5)\text{LiMO}_2$ $(M= \text{Ni, Mn, Co})$.

Employed a robotic approach to produce a “complete” compositional range to survey the properties of the LMR-NMC.
Approach

Modeling and Theory

This will include development of DFT models for the relevant material phases as identified by spectroscopy effort. In addition phenomenological (Newman) modeling will be used. Provides support for the diagnostics and synthesis efforts.

Previous work: LiMn$_2$O$_4$ was selected for theoretical studies of doped lithium transition-metal oxides see ES049
Approach

Characterization of the composite cathode materials.

we need to understand the nature of the cathode material when it is pristine, after the first charge and after continued cycling.

EXAFS data show that structural degradation see: ES049
Electrochemistry.

- We will develop a complete understanding of the electrochemistry of these materials.

**High Voltage Cycles**

- **Discharge**: 45 cycles
  - Voltage: 4.6 - 2.0 V (15 mA/g)
  - Capacity: 280 mAh/g

**Low Voltage Cycles**

- **Discharge**: Cycles 46 - 66
  - Voltage: 4.4 - 2.5 V (15 mA/g)
  - Capacity: 245 mAh/g

Voltage makes a difference: es019

The voltage profile changes are reflected in the dQ/dV plots – the “3V region” appears to grow at the expense of the “4V region”. The double-peak in the charge profile indicates distinct new crystal structures in the highly-cycled samples.

Project Id: ES032
**Approach**

**Synthesis**

Alternative synthesis are/will be needed to overcome the problems with the LMR-NMC materials. Key to the success of this initiative are materials synthesis and surface treatment techniques that can be employed to mitigate the structural changes present in the LMR-NMC materials.

**Complex Synthesis = Complex Structures**

- **Co-precipitation**
  - Process: $\text{M}_n\text{SO}_4 + \text{NaX} \rightarrow \text{Na}_2\text{SO}_4 + \text{MX}$
  - Notes: $X = (\text{OH})_2, \text{CO}_3, \text{C}_2\text{O}_4$
  - Ensures good mixing of transition metals

- **Solid State Synthesis**
  - Process: $\text{M}_n\text{X} + \text{A}_2\text{CO}_3 \rightarrow \Delta \rightarrow \text{H}_2\text{O}/\text{CO}/\text{CO}_2$ + $\text{AMO}_n$
  - Notes: Produces thermodynamically stable metal oxides

- **Ion-exchange**
  - Process: $\text{AMO}_n + \text{AZ} \longleftrightarrow \text{AMO}_n + \text{AZ}$
  - Notes: Low-temperature reaction can access metastable structures
Post treatment/system level fixes

- An alternative to the synthesis “fix” is changes to the material that helps mitigate the voltage fade. These are changes to the LMR-NMC material after it has been prepared, such as coating or physical changes.

\[(\text{Li}_{1.2}\text{Mn}_{0.52}\text{Ni}_{0.18}\text{Co}_{0.10}\text{O}_2)/\text{LiNiPO}_4\]

‘Li-Ni-PO\textsubscript{4}’ treatment protects surface below 5.0 V

Voltage fade is less in treated electrodes but still significant
Facilities will play a key role in solving voltage fade

- Materials scale-up
- Full cell builds and testing
- Post-test understanding
Future work

- Understand the cause of voltage fade.
  - Select most promising compositions/chemistries for exhaustive electrochemical evaluation and characterization of their chemical, physical and thermal properties;
  - Evaluate electrodes in a full lithium-ion cell configuration.
- Collaboration
  - Collaborate with other ABR participants, academic and industrial partners to understand and combat voltage fade phenomena and the cause thereof.

- On going down select to focus on solutions
Summary

- New program down selected to deal with voltage fade in LMR-NMC

- Many questions are still to be answered and we have established a comprehensive approach to solving the problem.
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