Electrochemical energy storage at ANL

Highlight of potential BMS challenges originating from advanced materials

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Argonne’s Energy Storage Mission

Argonne National Laboratory and JCESR bring together global leaders in energy-storage R&D

Approximate FTEs in parenthesis
Electrochemical Energy Storage at Argonne

U.S. DOE-EERE: Vehicle Technology Program
Key member of the Applied Battery Research (ABR) for Transportation Program

U.S. DOE-SC: Basic Energy Sciences
Energy Innovation Hub

Energy Frontier Research Center
Center for Electrical Energy Science (CEES)

Scientific User Facilities

Home to the Materials Engineering Research (MERF), Cell Fabrication (CFF), and Post-Test (PTF) Facilities as well as Electrochemical Analysis and Diagnostics Lab (EADL)
Electrochemical Energy Storage at Argonne

Capabilities span entire R&D spectrum: Core Competency is Materials Chemistry

Li$_2$MnO$_3$  \hspace{1cm}  Li$_{1.2}$Co$_{0.4}$Mn$_{0.4}$O$_2$

\[0.3Li_2MnO_3 \cdot 0.7Li[Mn_{0.5}Ni_{0.5}]O_2\]

\[\text{Voltage (V)}\]
\[\text{Capacity / mAh/g}^{-1}\]
USABC EV targets require new materials

• $125/kWh_{use} pack level

• BatPaC model enables quantification of new materials
  www.cse.anl.gov/batpac

• Silicon composite anode
• High capacity cathode
  - lithium & manganese rich LMR-NMC cathodes
Promise of LMR-NMC positive electrodes

- $x\text{Li}_2\text{MnO}_3\cdot(1-x)\text{LiMO}_2$ materials are under development worldwide to increase energy density and lower cost
  - Hypothesis: $\text{Li}_2\text{MnO}_3$ increases the stability of the layered structure
  - Thus, allowing access to higher reversible capacities

- High capacity shows synergy with advanced Li-ion negative

- Rich in manganese lowering $$/kg

- High in energy lowering $$/kWh
Tailor $\text{Li}_2\text{MnO}_3$ content to optimize Wh/kg

- $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$
  - $x = 0$
    - 160 mAh/g, 3.78 $U_{\text{ave}}$ vs Li
    - 605 Wh/kg vs Li
  - $x = 0.1$
    - 225 mAh/g, 3.81 $U_{\text{ave}}$ vs Li
    - 857 Wh/kg vs Li
  - $x = 0.3$
    - 260 mAh/g, 3.67 $U_{\text{ave}}$ vs Li
    - 954 Wh/kg vs Li
  - $x = 0.5$
    - 275 mAh/g, 3.58 $U_{\text{ave}}$ vs Li
    - 985 Wh/kg vs Li

- Capacity and voltage tradeoff
  - $x\text{Li}_2\text{MnO}_3$ between 0.1 to 0.4 may be best

DOE-EERE Vehicle Technologies Program

Voltage Fade and Hysteresis in LMRNMC

20 mA/g, HE5050 22C

OCV function & battery management

- Hysteresis has been dealt with before (NiMH)

- What about changing OCV function?

- If the OCV function change is predictable, then manageable?
  - Of course material still must show technological relevance!
De-convolute electrochemistry through cycling windows

Li$_{1.0}$Mn$_{0.50}$Ni$_{0.50}$O$_x$

$x = 0$

I

II

III

4.7 V

4.1 V

3.7 V

Cell Voltage (V)

2.0 2.5 3.0 3.5 4.0 4.5 5.0

Li$_{1.1}$Mn$_{0.55}$Ni$_{0.45}$O$_x$

$x = 0.1$

4.7 V

4.1 V

3.7 V

Cell Voltage (V)

2.0 2.5 3.0 3.5 4.0 4.5 5.0

Li$_{1.3}$Mn$_{0.65}$Ni$_{0.35}$O$_x$

$x = 0.3$

4.7 V

4.1 V

3.7 V

Cell Voltage (V)

2.0 2.5 3.0 3.5 4.0 4.5 5.0

Li$_{1.5}$Mn$_{0.75}$Ni$_{0.25}$O$_x$

$x = 0.5$

4.7 V

4.1 V

3.7 V

Cell Voltage (V)

2.0 2.5 3.0 3.5 4.0 4.5 5.0
X = 0.5 (Li_{1.2}Ni_{0.2}Mn_{0.6}O_2) measured after cycling

After activation

After 15 cycles

After 27 cycles
Increasing Li$_2$MnO$_3$ increases hysteresis and voltage fade

Increasing Li$_2$MnO$_3$ increases hysteresis and voltage fade.
Voltage Profile De-convolution

charge profile: constant current, vs. LTO

\[ C_{\text{cell}} \ (F) \]

\[ \Phi_{\text{cell}} \ (V) \]
Voltage Profile De-convolution

- charge profile: constant current, vs. LTO
- model fit

$C_{\text{cell}}$ (F) vs. $\Phi_{\text{cell}}$ (V)
Voltage Profile De-convolution

charge profile: constant current, vs. LTO
model fit

low voltage

$C_{\text{cell}}$ (F) vs. $\Phi_{\text{cell}}$ (V)

Voltage Profile De-convolution

Charge profile: constant current, vs. LTO
Model fit

$C_{\text{cell}}$ (F) vs. $\Phi_{\text{cell}}$ (V)

- Low voltage
- Moderate voltage

Voltage Profile De-convolution

- charge profile: constant current, vs. LTO
- model fit

\[ C_{\text{cell}} \text{ (F)} \]

\[ \Phi_{\text{cell}} \text{ (V)} \]

- low voltage
- moderate voltage
- extra capacity

Voltage Profile De-convolution

- charge profile: constant current, vs. LTO
- model fit

Evolution with cycle number?

Voltage Profile De-convolution: cycle 100

- charge profile: constant current, vs. LTO
- model fit

$C_{\text{cell}}$ (F)

$\Phi_{\text{cell}}$ (V)

- low voltage
- moderate voltage
- extra capacity

Voltage Profile De-convolution: cycle 200

- charge profile: constant current, vs. LTO
- model fit

- low voltage
- moderate voltage
- extra capacity

$C_{\text{cell}}$ (F)

$\Phi_{\text{cell}}$ (V)
Voltage Profile De-convolution: cycle 300

- charge profile: constant current, vs. LTO
- model fit

\[ C_{\text{cell}} \text{ (F)} \]

\[ \Phi_{\text{cell}} \text{ (V)} \]

- low voltage
- moderate voltage
- extra capacity

Voltage Profile De-convolution: cycle 400

- charge profile: constant current, vs. LTO
- model fit

\[ C_{\text{cell}} \quad (\text{F}) \]

\[ \Phi_{\text{cell}} \quad (\text{V}) \]

- low voltage
- moderate voltage
- extra capacity
Voltage Profile De-convolution: cycle 500

- charge profile: constant current, vs. LTO
- model fit

\[ C_{\text{cell}} \text{ (F)} \]

\[ \Phi_{\text{cell}} \text{ (V)} \]

- low voltage
- moderate voltage
- extra capacity

Voltage Profile De-convolution: cycle 500

- charge profile: constant current, vs. LTO
- model fit

$C_{\text{cell}} \, (\text{F})$

$\Phi_{\text{cell}} \, (\text{V})$

- low voltage
- moderate voltage
- extra capacity

Evolutionary trends?

theory $\rightarrow$ exponential growth law
with maximal voltage fade capacity
Extracted Trend: Exponential Growth Law

theory → exponential growth law with maximal voltage fade capacity

Maximal voltage fade capacity is approximately 20% of initial total capacity

Growth law holds for different cycling currents

theory → exponential growth law
with maximal voltage fade capacity

But rate constant is a function of current density used in cycling

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