Impact of Ni content on interface reactions at NCM electrodes

D. Streich\textsuperscript{a}, F. Chesneau\textsuperscript{a}, A. Guéguen\textsuperscript{a}, M. Mendez\textsuperscript{b}, M. He\textsuperscript{a}, C. Bolli\textsuperscript{a}, P. Novák\textsuperscript{a}, E. J. Berg\textsuperscript{a}

\textsuperscript{a}Paul Scherrer Institute, Electrochemistry Laboratory, CH-5232 Villigen PSI, Switzerland
\textsuperscript{b}BASF SE, GCN/EE – M311, 67056 Ludwigshafen, Germany

Motivation / Objectives

Motivation:
Layered nickel cobalt manganese oxides (NCM) have been and will likely increase to be of high commercial attractiveness as cathode materials for high-end Li-ion batteries\cite{1}. The partial substitution of Co renders NCMs less costly than LiCoO\textsubscript{2} and, on top of this, the introduction of Ni has proven to result in higher reversible specific charge (~180 mAh g\textsuperscript{-1} vs. ~150 mAh g\textsuperscript{-1})\cite{2}. Cell performance on a series of layered oxides of varying Ni content (LiCoO\textsubscript{2}, NCM111, NCM622, NCM811), Celgard 2400 separator, Li metal foil anodes, and 1 M LiPF\textsubscript{6} in 3:7 (w/w) EC:DEC as electrolyte. Specific electrode surface areas and average potentials are also taken into our analysis.

Objectives:
1. Is there a correlation between CO\textsubscript{2} evolution and Ni content of NCMs?
2. Is it possible to prevent or reduce the extent of CO\textsubscript{2} evolution?

Approach / Instrumentation

Approach:
Many interface reactions result in the evolution of gaseous species. Therefore, we try to get a better understanding of these reactions by using online electrochemical mass spectrometry (OEMS) to quantitatively analyze specific gaseous species evolving from cells during electrochemical cycling. The investigated cells contain NCM (NCM111, NCM622, NCM811), Celgard 2400 separator, Li metal foil anodes, and 1 M LiPF\textsubscript{6} in 3:7 (w/w) EC:DEC as electrolyte. Specific electrode surface areas and average potentials are also taken into our analysis.

Instrumentation:

Conclusions / Open issues

A strong correlation between CO\textsubscript{2} evolution and Ni content exists in the first cycle at voltages > 4.3 V.

For state-of-the-art, commercially relevant cell voltages ≤ 4.3 V, the correlation is weak and cycle-independent suggesting that surface reactivity of the NCM materials is low.

It needs to be further investigated whether the cycle-dependent loss of correlation at potentials > 4.3 V originates from interface reactivity changes or from bulk effects.

NCM811 exhibits the highest specific energy of all tested NCM materials at CO\textsubscript{2} evolution rates barely higher than LiCoO\textsubscript{2}.

Low CO\textsubscript{2} evolution of Ni-rich NCM materials such as NCM811 can be further extended to even higher potential by tailoring the material.

It remains unclear whether a reduction in early cycle CO\textsubscript{2} evolution would improve long term cell performance.

The gassing observed in the first cycle could be irrelevant for a commercial cell where a degassing step after formation is standard.

References


[3] W. Noh et al., Journal of Power Sources, 2013, 233, 121-130: «Comparison of the structural and electrochemical properties of layered Li(Ni,Co,Mn)O\textsubscript{2} (x = 1/3, 0.5, 0.6, 0.7, 0.8, 0.85) cathode material for lithium-ion batteries».

OEBS results

Correlation between CO\textsubscript{2} evolution and Ni content

- Minor dependence on Ni content up to 4.3 V; no difference between 1\textsuperscript{st} and 2\textsuperscript{nd} charge.
- Inset: attractive gain in specific energy with Ni content; CO\textsubscript{2} evolution rate of NCM811 barely higher than LiCoO\textsubscript{2} up to 900 mWh g\textsuperscript{-1}.
- Strong dependence on Ni content between 4.3 and 4.7 V.
- Dramatic decrease in slope after 1\textsuperscript{st} cycle.
- Decrease of similar magnitude after the 2\textsuperscript{nd} cycle → slope(4.3 - 4.7 V) ≈ slope( - 4.3 V)

Prevention or reduction of CO\textsubscript{2} evolution

- 1\textsuperscript{st} charge: 50% reduction.
- 2\textsuperscript{nd} charge: 33% reduction.

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