

Low-Temperature Study of Lithium-Ion Cells Using a LiSn Micro-Reference Electrode

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Introduction

Lithium-ion batteries are receiving much interest for use in hybrid electric vehicles (HEVs), which require high power. While lithium-ion batteries have abundant power at room temperature, their power is poor at the low temperatures that HEVs experience in normal use, and the concern exists that lithium metal could plate on the negative electrode during charge pulses. The goal of this work is to determine the impact that active material has on low-temperature performance using a Li_xSn *in situ* micro-reference electrode over a wide temperature range of 45°C to -30°C.

Argonne's Approach

The electrochemical processes taking place on the negative and positive electrodes were investigated using *in situ* micro reference electrodes (REs) that we developed earlier in our advanced battery work. The micro RE consists of a 1- μm -thick tin coating on a 25- μm -diameter copper wire that is coated with an insulating polyurethane coating. A 1-cm length of the polyurethane coating is removed prior to use to expose the tin surface. A cell is assembled with the micro RE placed between two layers of separator in the cell and then charged with lithium from either electrode.

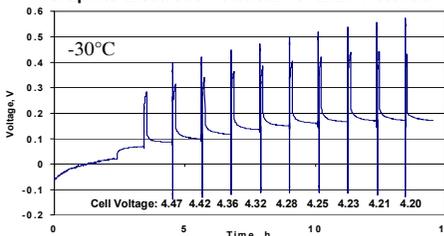
Constant current cycling and pulse-power tests are performed on lithium-ion cells with varying compositions at decrements of 10 to 15°C from 45°C down to -30°C. Electrochemical impedance spectroscopy (EIS) studies are performed on these cells over a frequency range of 60 kHz to 2 mHz.

A variety of active materials were used as electrodes in this study. The electrolyte was 1.2 M LiPF_6 in EC:EMC (3:7 by wt.) with Celgard 2325 as the separator.

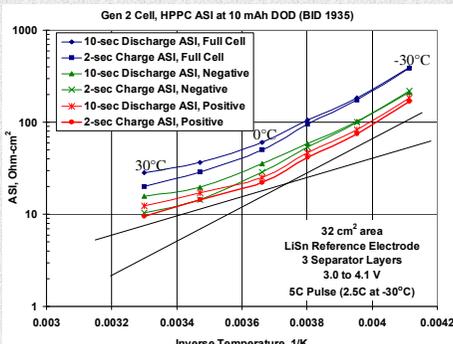
Physical properties of active materials used in this study.

Active Material	Particle Size D50 / D90, μm	Surface Area m^2/g (BET)	Comments
GMCF Petco Ltd.	13 / 35	2.8	MELBLON Milled Fiber, Meso-phase pitch graphite
MCMB-25-28 Osaka Gas Chemicals	22.4 / 37.0	0.85	Spherical graphite beads
GDR-AA-3-3 MITSUBI Mining Co.	16.2 / 21.1	3.2	Carbon-coated natural graphite
MAG-10 Hitachi Chemical Co.	10.1 / 21.4	5.2	Synthetic graphite, Gen2 Negative
MCMB-10-28 Osaka Gas Chemicals	11.82	2.01	Synthetic graphite, Gen3 Negative
LINILITE CA1505N Fuji Chemical Ind.	10.3 / 17.1	0.78	Gen2 Positive $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$
L333B Seimi	12.2	0.41	Gen3 Positive $\text{Li}(\text{Li}_{1-x}\text{Mg}_x\text{Co}_y\text{Mn}_{1-y})\text{O}_2$

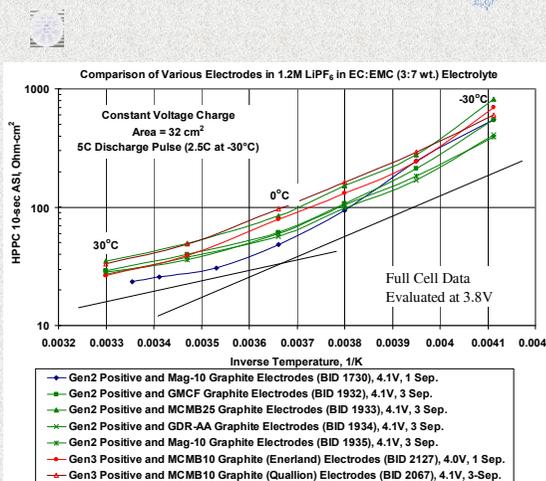
Graphite Electrode Potential vs. Li/Li^+ Potential



The potential of the graphite negative electrodes used in this study does dip below lithium potential not only during charge pulses, but also under normal charging if the cell cutoff voltage is not reduced from its room temperature setting of 4.1 V. Cells based on hard carbon as the negative electrode are much less likely to deposit lithium because hard carbon operates at potentials 200 to 800 mV above lithium potential, whereas graphite has a long voltage plateau only 100 mV above lithium potential.

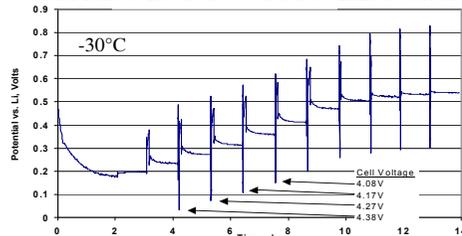


Pulse power impedance increases abruptly below 0°C due to almost equal contributions from the negative (Mag-10 graphite) and positive ($\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) electrodes. Results were similar for other electrodes.



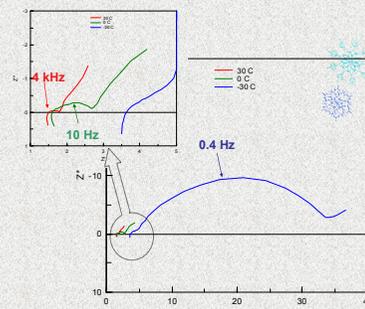
Similar trends were observed for various electrode combinations in the same electrolyte. Two Arrhenius regions appear to exist with a crossover around 0°C. This was also observed for other electrolytes.

Hard Carbon Electrode Potential vs. Li/Li^+ Potential

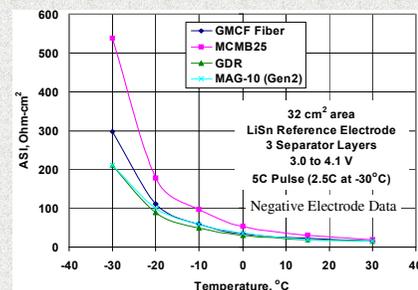


Challenges

Many researchers have attempted to improve the low-temperature performance of lithium-ion batteries by developing electrolytes with high ionic conductivities at low temperature. However, when these electrolytes were used in actual full cells, there was only a marginal improvement in performance. Clearly, another mechanism was at work. An *in situ* technique was needed that could elucidate the reason for the poor low-temperature performance.



Electrochemical impedance spectroscopy data for a lithium-ion full cell indicates a large increase in interfacial impedance at low temperature. Similar trends were observed for the positive and negative electrodes.



HPPC 10-sec discharge pulse ASI for the graphite electrodes versus Gen2 Positive showing a likely influence of surface area.

Conclusions

The most surprising finding from this work was that the impedance rise at low temperature was not significantly impacted by the choice of active material. The main rise in impedance occurs in the mid-frequency range. Processes that occur in this frequency range are generally interfacial in nature. Materials with high surface areas do appear to help the power performance at low temperature, but this is only part of the solution. Cells based on hard carbon (and $\text{Li}_4\text{Ti}_5\text{O}_{12}$) as the negative electrode were much less likely to deposit lithium because they operate at potentials well above lithium potential. Efforts are underway to investigate the influence of electrolyte properties.