

Improved conductive carbon additives for high-energy lithium-ion batteries

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Small-sized lithium ion batteries for portable electronic devices are considered a mature technology, large-scale electric storage devices for transportation applications still require significant improvements of the battery energy density to cost ratio.[1] One promising approach involves development of positive electrode materials that can store more charge and/or operate at higher potentials. e.g., $x\text{Li}[\text{Mn}_{1/2}\text{Ni}_{1/2}]\text{O}_2$ $y\text{LiCoO}_2$ $z\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ ($x + y + z = 1$), $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. [2, 3]

Carbon black (CB) conductive additives are key components of all Li-ion composite cathodes. CB additives primary role is to enhance electronic percolation in the composite and reduce ohmic resistance of the electrode. Interestingly, carbon black additives constitute the majority of the electrode surface area. Unfortunately, at high potentials CB becomes electrochemically active toward electrolyte oxidation and anion intercalation, which results in material degradation, surface layer formation, electrode impedance rise and battery failure.

This work focuses on the electro-catalytic properties of carbon blacks and remedies to mitigate their interfacial activity in high-energy Li-ion systems.

A thermal treatment to suppress CB electrochemical activity in organic electrolytes and to inhibit adverse side effects was developed and tested both with model carbon black materials and commercial carbon black additives.

Pristine and heat-treated pyrolyzed polyimide model samples of carbon black were investigated towards their electrochemical reactivity at elevated potentials (exceeding 4.5 V vs. Li/Li^+), using cyclic voltammetry (CV), potentiostatic step investigations and charge-discharge profile simulations.

The beneficial effect of the heat treatment was confirmed and the procedure was applied to a commercial carbon black powder, Super P[®] Li from Timcal. Figure 1 depicts the CV of the pristine (red lines) and the heat treated CB (blue lines) electrodes normalized with regards to the surface area.

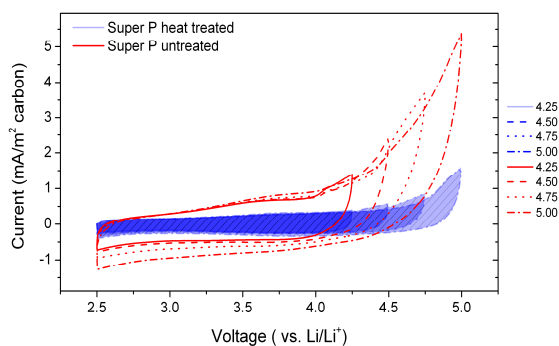


Figure 1: Cyclic voltammogram of the pristine (red) and the heat treated CB (blue), counter and reference electrode metallic lithium, scan speed 5 mV/s, electrolyte EC:DEC 1M LiPF_6

The improved carbon black additives displays a significantly lower the reactivity (by a factor of 7) toward the electrolyte, even though the surface area of the CB is slightly increased after the treatment.

To demonstrate the beneficial effect of the improved carbon black, composite electrodes with $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ (Umicore MX-6) and $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.10}\text{Mn}_{0.55}\text{O}_2$ (Toda HE5050) were manufactured and their electrochemical behavior evaluated.

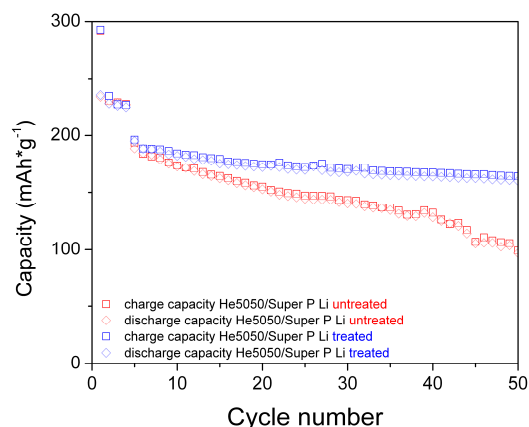


Figure 2: Charge/discharge capacity vs. cycle number of composite electrodes in coin cells (Toda He5050/PVdF/CB) utilizing treated (blue) or pristine (red) CB, counter and reference electrode metallic lithium; 4 cycles with C/12, then C/3; electrolyte EC:DEC 1M LiPF_6

Composite cathodes utilizing the heat-treated CB display a prolonged lifetime and, in the case of the He5050 active material, also an improved coulombic efficiency.

Acknowledgement

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References

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