



Short communication

Continuity and performance in composite electrodes

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ABSTRACT

It is shown that the rate performance of a lithium battery composite electrode may be compromised by poor internal connectivity due to defects and inhomogeneities introduced during electrode fabrication or subsequent handling. Application of a thin conductive coating to the top surface of the electrode or to the separator surface in contact with the electrode improves the performance by providing alternative current paths to partially isolated particles of electroactive material. Mechanistic implications are discussed and strategies for improvement in electrode design and fabrication are presented.

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1. Introduction

A typical cathode material used in a rechargeable lithium battery has an electronic conductivity in the range of 10^{-3} to 10^{-9} S cm^{-1} . Composite electrodes are manufactured by slurry casting of a mixture of the active material, an electronic conductor such as carbon, and a binder onto a metal current collector. It has been shown that the electronic conductivity of the composite electrode plays a critical role in battery performance [1–3]. Ideally, the carbon is distributed uniformly and forms a conducting network between the active particles. In practice, however, the distribution of solids is non-uniform on both small and large scales [4,5]. Initial inhomogeneity may be caused by agglomeration of particles [6] and by differential settling during electrode casting and drying [7]. This leads to non-uniformity of mechanical strength and electronic conductivity within the electrode. Some inhomogeneity may also be introduced by binder redistribution during drying, by calendaring, by cutting, winding, and compacting of assembled cells, and by changes in binder rheology, volume, and adhesion during electrolyte filling. These influences may introduce or exaggerate cracks and gaps in the composite electrode that contribute to non-uniform connectivity and inhomogeneous current distribution, and can even lead to electronic disconnection of portions of the electrode. Here we provide evidence for inhomogeneity and poor electronic connectivity within calendared composite electrodes. Their effects on rate capability are demonstrated through

comparison of untreated electrodes with electrodes to which a thin conducting top layer has been added before testing. A simple model for the electrode morphology and a plausible mechanism by which the topcoat improves their performance are proposed.

2. Experimental

LiFePO₄ composite electrodes comprised of 82 wt% carbon-coated LiFePO₄, 4 wt% carbon black, 4 wt% graphite and 10 wt% polyvinylidene difluoride (PVDF) binder on a carbon-coated aluminum current collector were obtained from a commercial supplier. LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ cathode laminates, supplied by the USDOE Advanced Technology Development program, contained 84 wt% LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ powder (Fuji CA1505), 4 wt% amorphous carbon (Chevron), 4 wt% graphite (SFG-6, Timcal) and 8 wt% PVDF binder (Kureha KF-1100). Both electrodes had been densified by calendaring after initial casting and drying. Cathode disks with an area of 1.6 cm² were cut from the electrode sheets and assembled into Swagelok[®]-type cells with Li foil counter and reference electrodes, Celgard 3401 separators, and 1 M LiPF₆ in 1:1 ethylene carbonate:propylene carbonate (Ferro Corporation) electrolyte. The cells were assembled and sealed in an argon-filled glove box (O₂ < 1 ppm, H₂O < 2 ppm), and were subjected to charge and discharge cycling at various rates using an Arbin battery-testing system. Impedance measurements were carried out after rate testing, in the frequency range between 10⁶ kHz and 0.05 Hz using a 10 mV sinusoidal perturbation (Solartron 1250/1280).

Some of the cathode disks were coated with a layer of Au (Aldrich, 99.99%) using a vacuum sputter coater (SCD 050, BAL-TEC) at room temperature. The current was set to 40 mA under a work-

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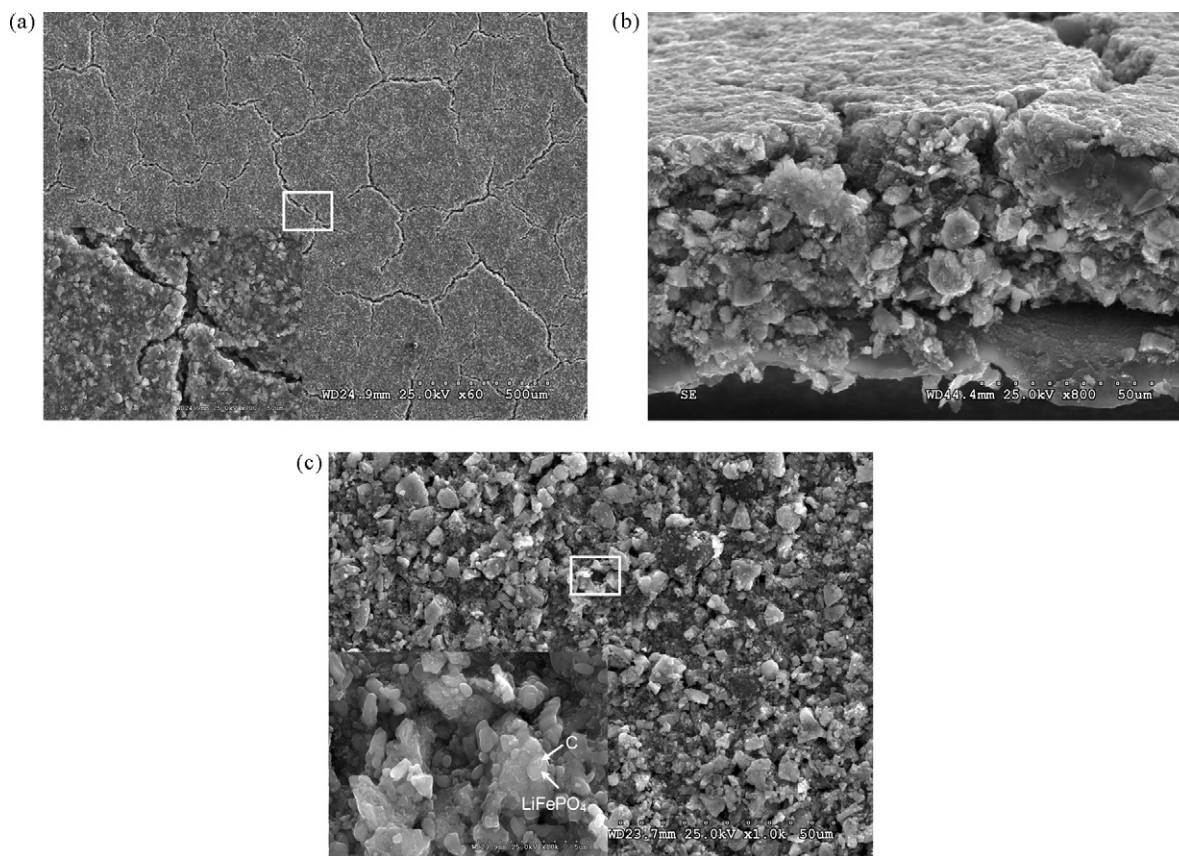


Fig. 1. SEM images of as-received LiFePO₄ composite electrodes: (a) top and (b) side views of a 50 μm-thick electrode; (c) top view of a 150 μm-thick electrode.

ing pressure lower than 0.05 mbar. The thickness of the coating was controlled by varying the sputtering time based on calibration with a flat substrate. In the same way, separator disks (2.8 cm²) were coated on one side with a layer of Au. Cathodes were carbon-coated by airbrushing with a suspension of carbon black in acetone. Scanning electron microscopy (SEM) images were collected using a Hitachi S-4300 SE/N microscope operating at 25 kV.

3. Results and discussion

3.1. Conductive coating on electrode surface

SEM images of two calendared, fresh LiFePO₄ electrodes are shown in Fig. 1. Fig. 1a and b is the top and side views of a 50 μm-thick electrode with an active material loading of 5.37 mg cm⁻². Numerous cracks of various sizes are visible, some of which extend from the surface of the electrode to the current collector and segregate the composite electrode into disconnected islands. The material distribution is also inhomogeneous, as particles of the active material and carbon are separated from one another. Fig. 1c shows the top view of a thicker (150 μm) LiFePO₄ electrode with an active material loading of 15.92 mg cm⁻². Here, particle segregation due to differential settling is more evident than in the thinner electrode. The top surface of this electrode consists mostly of large, irregularly shaped active material particles, with only a small amount of carbon visible.

The charge and discharge performances of both LiFePO₄ laminates with 20 nm Au coatings were compared with those of untreated electrodes (Fig. 2). The cells were galvanostatically charged and discharged for five cycles each at C/8, C/4, C/2, C and 3C, between 2.5 and 4.0 V. At C/8, the untreated 50 μm-thick cathode delivered a discharge capacity of 130 mAh g⁻¹, while the Au-coated

electrode delivered 145 mAh g⁻¹. At 3C, the discharge capacity was only 95 mAh g⁻¹ for the plain electrode and 115 mAh/g for the Au-coated electrode. The Au topcoat improved the low rate capacity of the LiFePO₄ electrode by 11% and high rate capacity by 21%. Similar improvement was obtained with the 150 μm-thick electrode, with the discharge capacity increasing 14% at C/8 and 26% at 3C.

A similar comparison was made between as-received and Au-coated LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ electrodes. At cycling rates of C/5, C/2, C, 2C and 3C, the cathode with a 20 nm Au topcoat delivered

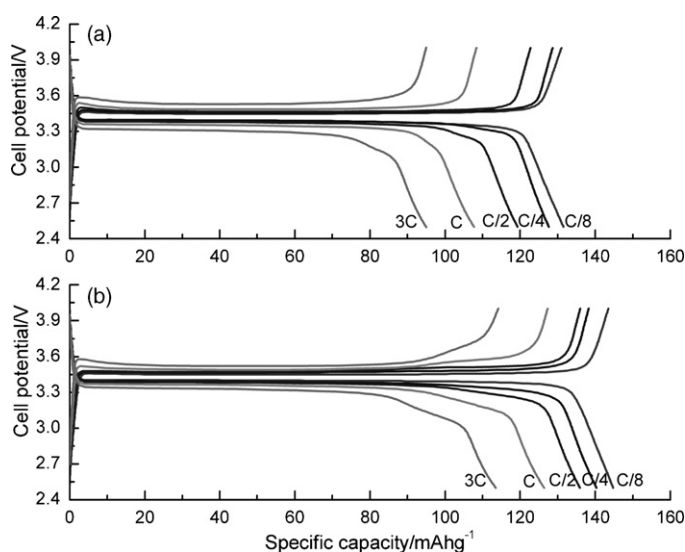


Fig. 2. Electrochemical charge and discharge profiles of cells with (a) untreated LiFePO₄ cathode; (b) LiFePO₄ cathode coated with 20 nm of Au.

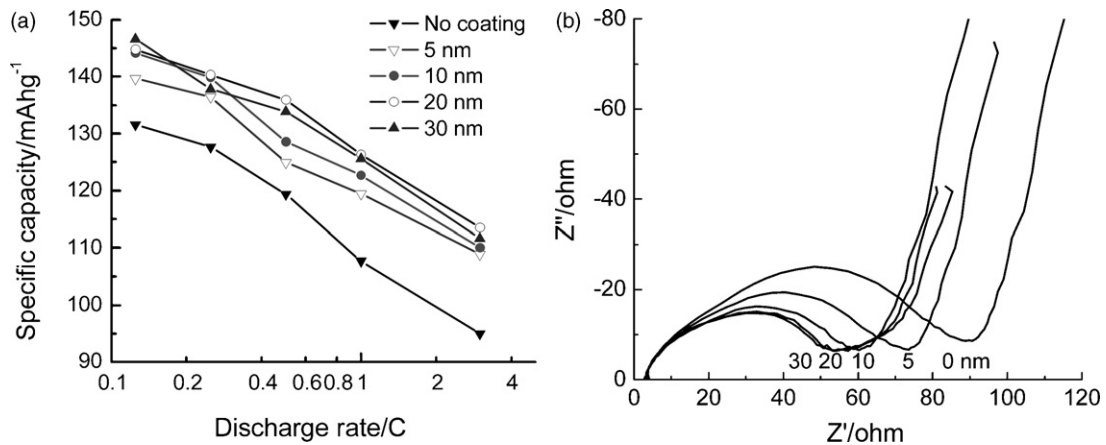


Fig. 3. (a) Rate capability comparison of LiFePO₄ electrodes with various thickness of Au topcoat; (b) Nyquist plots of cell impedance measured after the rate cycling tests. Electrode area: 1.6 cm².

8% more capacity than the plain LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ electrode, indicating improved utilization of the electrode, indicating improved utilization of the electrode. In contrast to the LiFePO₄ electrode, the capacity improvement was not rate-dependent. This is most probably due to the higher electronic conductivity and better intrinsic rate capability of this cathode material as compared to LiFePO₄.

To study the effect of Au coating thickness, a series of 50 μm-thick LiFePO₄ electrodes was prepared with Au coatings of 5, 10, 20, and 30 nm. The discharge profiles of as-received and Au-coated LiFePO₄ electrodes at different cycling rates are shown in Fig. 3a. Performance improvement was observed on all electrodes with Au coatings, the extent of the improvement varying with cycling rate. Up to a thickness of 20 nm, the discharge capacity increased with increasing Au topcoat thickness. Although the electrode with a 30 nm Au topcoat had a slightly higher capacity than the one with a 20 nm coating at the low rate of C/8, its capacity was lower at rates above C/8. It may be that the thicker Au layer blocked access of Li⁺ ions to some active material surfaces.

After the variable rate tests, electrochemical impedance spectra (EIS) were measured. In the Nyquist plots shown in Fig. 3b, the diameter of the depressed semicircles in the high frequency region corresponds to the charge transfer resistance in the LiFePO₄ electrodes [8–10]. The uncoated electrode had a resistance of 90 Ω. This decreased with increasing Au topcoat thickness up to 20 nm, where the resistance was 45% lower than for the uncoated electrode, but no further decrease was observed for the 30 nm coating. This clearly indicates improved conductivity of Au-coated electrodes.

As a possible practical treatment to improve the conductivity of composite electrodes, we investigated the feasibility of using carbon for the topcoat. A 10 nm layer of carbon black was applied to the surface of an LiFePO₄ electrode by airbrushing with an acetone suspension. Its rate capability was compared to the uncoated LiFePO₄ electrode and the electrode with 20 nm Au coating (Fig. 4). Improved performance was observed at all rates for the carbon-coated electrode. At 3C, the discharge capacity was 15% higher than that of the uncoated LiFePO₄ electrode, but 6% lower compared to the best Au coating. The carbon coating is less conductive than Au, but did not appear to block electrolyte access at any thickness.

3.2. Conductive coating on separator

To determine whether these conductive coatings work by enhancing the connectivity between neighboring particles on the electrode surface or by connecting larger sections of the electrode to one another and to the current collector, we investigated the effect of applying a conductive coating to the separator surface in

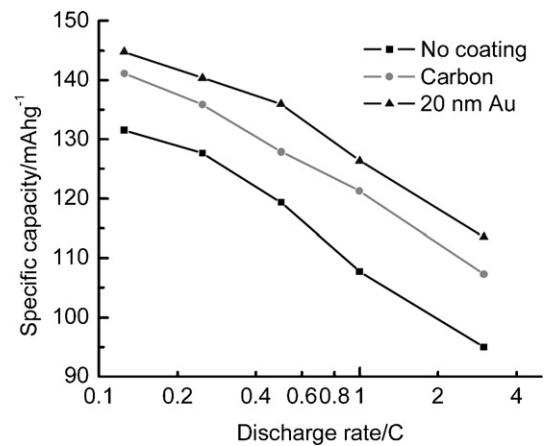


Fig. 4. Rate capability of LiFePO₄ cathodes with indicated surface coatings.

contact with the cathode. A 5 nm layer of Au was applied to one side of a Celgard separator and a cell was assembled with the conductive coating facing the LiFePO₄ electrode. Only a thin layer was used to avoid pore blocking and/or electronic shorting through the separator. Fig. 5 shows the rate performance of a reference cell with an untreated LiFePO₄ cathode and Celgard separator, a cell with a LiFePO₄ cathode coated with 20 nm of Au and a plain separator, and a cell with an untreated cathode and a coated separator. Com-

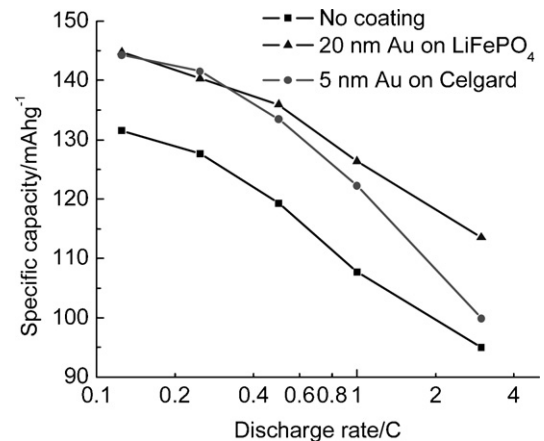


Fig. 5. Rate capability comparison of the cells with Au coating on the cathode vs. on the separator.

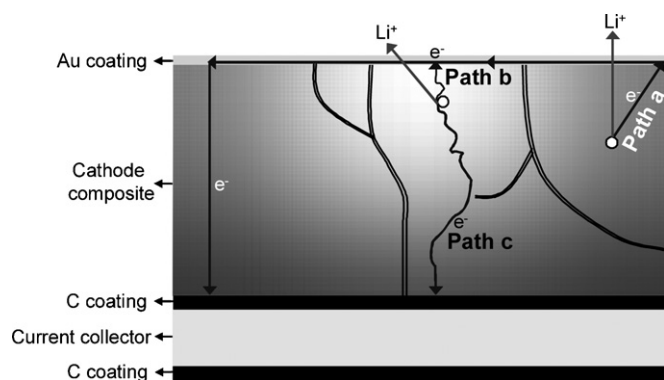


Fig. 6. Schematic diagram of the conduction paths in Au-coated composite electrode. The spheres represent active material particles, and lines within the composite layer represent cracks in the electrode.

pared with the reference cell, both cells with Au coatings delivered higher discharge capacity. At low rates, the performance improvements were similar, but above $C/2$, the cell with a coated cathode had superior performance. This suggests that both mechanisms, better electronic contact between LiFePO_4 particles and introduction of a secondary current path to partially isolated parts of the electrode are operative.

3.3. Mechanism

The rate improvements provided by surface conductive coatings result from improved electronic conduction paths within the porous electrodes (Fig. 6). The imperfections in the electrode are represented by randomly distributed cracks and the variation in the dark shade intensity that corresponds to the non-uniform distribution of carbon additive. The active reaction sites for lithium insertion or extraction entail both Li^+ and e^- . Particles close to the electrode surface have the shortest Li^+ diffusion distance, but electrons have to travel the farthest to or from the current collector. Due to differential particle settling, some particles near the surface are electronically poorly connected. In the presence of cracks, some of the active material may be isolated due to interruption of the electron path.

When a conductive layer is applied to the electrode surface, additional electron paths are created. This makes it possible to access isolated active material (shown as Path a), which results in improved utilization and higher total capacity. The highly conductive surface coating also provides alternative electron paths with lower resistance (Path b vs. Path c), which improves the rate capability of the electrode. The level of improvement achieved depends on the condition of the electrode, i.e. the number and the location of cracks, uniformity in the distribution of active material and carbon, particle sizes and shape variations in the active material. Because it is practically impossible to make a composite electrode

that is perfectly uniform and defect-free, commercial electrodes might benefit from such a treatment. Electrodes made from materials with low intrinsic electronic conductivity, such as LiFePO_4 , likely would benefit most. A thin layer of carbon black with a small amount of binder, for example, could be applied during slurry coating or following a drying step without adding significant cost or complexity. It has been reported that carbon particles on the cathode surface can migrate through the separator during cycling, a process known as carbon retreat [11]. This affects the connectivity between particles and decreases the conductivity of the electrode, contributing to capacity and power fade. Application of a conductive topcoat could effectively extend the lifetimes of cells in which this mechanism plays a role.

4. Conclusions

The observed improvement in utilization and rate performance caused by introduction of a conductive coating on or in contact with the top surface of a composite electrode demonstrates the presence of inadequate connectivity within the electrode and partial isolation of some of the active material. An approach is suggested to improve the conduction paths and performance of composite electrodes by application of an additional conductive coating to create additional electronic paths, improving utilization of the electrode active material by accessing isolated particles, and increasing rate capability by exploiting electronic paths with lower resistances.

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