Optimization of Acetylene Black Conductive Additive and PVDF Composition for High-Power Rechargeable Lithium-Ion Cells

G. Liu, a,b,2 H. Zheng, a,c A. S. Simens, b,d A. M. Minor, b X. Song, a and V. S. Battaglia a,b

a Lawrence Berkeley National Laboratory, Energy Technologies Division and b National Center for Electron Microscopy, Material Science Division, Berkeley, California 94720, USA

Fundamental electrochemical methods were applied to study the effect of the acetylene black (AB) and the polyvinylidene difluoride (PVDF) polymer binder on the performance of high-power designed rechargeable lithium-ion cells. A systematic study of the AB/PVDF long-range electronic conductivity at different weight ratios is performed using four-probe direct current tests, and the results are reported. There is a wide range of AB/PVDF ratios that satisfy the long-range electronic conductivity requirement of the lithium-ion cathode electrode; however, a significant cell power performance improvement is observed at small AB/PVDF composition ratios that are far from the long-range conductivity optimum of 1 to 1.25. Electrochemical impedance spectroscopy (EIS) tests indicate that the interfacial impedance decreases significantly with an increase in binder content. The hybrid power pulse characterization results agree with the EIS tests and also show improvement for cells with a high PVDF content. The AB to PVDF composition plays a significant role in the interfacial resistance. We believe the higher binder contents lead to a more cohesive conductive carbon particle network that results in better overall local electronic conductivity on the active material surface and, hence, reduced charge-transfer resistance.

© 2007 The Electrochemical Society. [DOI: 10.1149/1.2792293] All rights reserved.

Manuscript submitted June 17, 2007; revised manuscript received August 21, 2007. Available electronically October 22, 2007.

Lithium-ion rechargeable batteries are a prime candidate for electric vehicle (EV) and hybrid electric vehicle (HEV) applications due to their high-energy density and light weight. These applications, especially HEV, require low internal resistance for superb high-rate charge and discharge performance. The lithium-ion cell electrode is composed of active materials, conductive additives, and a polymer binder to combine the particles into an integrated electrode system. The cathode active material is made from metal oxide materials, which have very low intrinsic conductivity ranging from $10^{-3}$ S/cm for LiCoO$_2$ to $10^{-9}$ S/cm for LiFePO$_4$ at ambient condition. The active material primary particles are sintered into micrometer-size particles and mixed with highly conductive carbon additives to improve the particle conductivity. In this study, LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ is used as active material, acetylene black (AB) is used as conductive additive, and polyvinylidene difluoride (PVDF) is used as polymer binder. The focus here is the optimization of the composition of the porous composite electrodes to improve the lithium-ion cell performance.

A unique approach is taken to study the lithium-ion battery cathode electrode as a polymer composite. A simple cathode is a three-component composite including a polymer binder and two discreet sized particles: the nanosize AB and the microsize LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$. The specific surface area of the AB is at least ten times larger than that of the LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ material. In a polymer composite system, the surface area dominates the mixing process such that most of the polymer binder in a composite will associate with the smaller size conductive additive, even when the AB is far from being the weight-dominant component. In this respect, we view the electrode system as a LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ cathode material being bond together by an AB/PVDF composite. The electronic properties of the AB/PVDF composites naturally affect the performance of the electrode. In this report, a set of experiments were designed to evaluate the contribution of the long-range electronic conductivity of AB/PVDF composites to the overall electrode performance. The long-range electronic conductivities of the AB/PVDF composites and the AB/PVDF/active material composites were measured via four-point probe direct-current (dc) method. The composite films were cast on glass for the four-point probe dc measurements. Lithium-ion cells of very similar capacity and configuration but with various the AB/PVDF ratios were constructed, and their power performance evaluated with variable rate cycling, hybrid pulse power characterization (HPPC) experiments, and electrochemical impedance spectroscopy (EIS).

Most of the previous work on electrode compositions treats the conductive additive and binder as two independent variables: one present for providing electronic conductivity and the other present to hold the electrode components together. Although AB does provide electronic conductivity in the cathode electrode, long-range electron pathways cannot be formed without the participation of the binders. Therefore, AB and PVDF are the integrated parts of the electrode rather than two independent components. We report the electronic properties of the AB/PVDF composites and their effects to the electrode performance.

Experimental

Materials — Battery-grade AB with an average particle size of 40 μm and a material density of 1.95 g/cm$^3$ was acquired from Denka Singapore Private Limited. PVDF no. 1100 binder with a material density of 1.78 g/cm$^3$ was supplied by Kureha, Japan. Anhydrous N-methylpyrrolidone (NMP) was purchased from Aldrich Chemical Company. The AB/PVDF mixtures were made by dissolving 5 g of PVDF in 95 g of anhydrous NMP. A given amount of AB was dispersed in the PVDF polymer solution to meet the desired ratio. To ensure the thorough mixing of the AB nanoparticles into the polymer solution, sonication was used. A Branson 450 sonicator equipped with a solid horn was used. The sonication power was set at 70%. A continuous sequence of 10 s pulses followed by 30 s rests was used. The sonic dispersion process took ~30 min. The slurry properties for all AB/PVDF in NMP were constant after 20 min of sonication. Slurries with active cathode material were made by adding the targeted amount of LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ active material to the freshly premixed AB/PVDF/NMP slurry. The cathode slurry mixture was homogenizing using Polytron PT10-35 homogenizer at 3000 rpm for 15 min until a viscous slurry was acquired. LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ with a mean particle size of 10 μm and lattice density of 4.73 g/cm$^3$, was a gift from Toda, Japan. The manufacturer-suggested specific capacity is 173 mAh/g when cycled between 3 and 4.1 V.

* Electrochemical Society Active Member.
2 Permanent address: Henan Normal University, Henan Provence, China.
3 Present address: Material Science and Engineering Department, Stanford University, Stanford, California 94305, USA.
4 E-mail: Gliu@lbl.gov
Film and electrode casting.— In order to understand the conductive behavior of the AB/PVDF composite system, different weight ratios of AB are dispersed in PVDF-NMP solutions and cast into thin films. The film compositions extend from 1:10 to 1:1 AB/PVDF weight ratios. The films show cracks beyond the AB/PVDF ratio of 1:1, which would indicate that mixtures with less than this fraction of binder may not effectively maintain coherent, long-range conductivity in an electrode. AB/PVDF ratios greater than 1:1 will also likely result in mechanically weak composites. LiNi0.8Co0.15Al0.05O2 active material was mixed with the AB/PVDF to fabricate electrodes. The AB content was fixed at 4% by weight in three different electrode compositions, and the amount of PVDF binder was varied to achieve AB/PVDF weight ratios of 1:2, 1:1.25, and 1:1.

Both AB/PVDF and AB/PVDF/LiNi0.8Co0.15Al0.05O2 films for the four-point probe dc tests were cast onto glass surfaces with a doctor blade. Cathode laminates (AB/PVDF/LiNi0.8Co0.15Al0.05O2) for coin-cell testing were cast on 30 μm thick battery-grade Al sheet using a Mitutoyo doctor blade and a Yoshimitsu Seiki vacuum draw coater. The films and laminates were first dried under IR using a Mitutoyo doctor blade and a Yoshimitsu Seiki vacuum draw coater. The films and laminates were first dried under IR on an A-150 evaporator. Cathode laminates were sectioned they were then carbon coated to help dissipate charge. Imaging was done using a JEOL 200CX microscope operating at 200 kV. All imaging work was performed at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory.

Four-point probe dc testing.— The conductivities of both the AB/PVDF and AB/PVDF/LiNi0.8Co0.15Al0.05O2 films on glass substrates were measured using the four-point probe dc method.9 The dry film conductivities were measured after the films were dried in a vacuum oven overnight at 120°C. Afterward, the films were wetted with electrolyte solvent and their conductivities were measured again. The dc conductivity measurement was performed using a custom-built equal-distance linear four-point probe apparatus with a Solartron 1286 Electrochemical Interface and a CorrWare software package. A direct current is applied between the two outer probes; the voltage is registered between the two inner probes. The probes are spring loaded to ensure intimate contact between and probes and the film. The conductivity of each film was measured four times at different locations on the film with the standard deviations shown as error bars. Electrolyte solvent was made by mixing 1:1 weight ratio of ethylene carbonate (EC) and diethyl carbonate (DEC) for the four-probe dc test. No salt was added to the electrolyte solvent to prevent ion interference with the measurements. The film was submerged in the electrolyte solvent, and the conductivity measurements were repeated, intermittently, until a constant value was obtained.

Results and Discussion

DC conductivities of AB/PVDF and AB/PVDF/LiNi0.8Co0.15Al0.05O2 cast films.— Figure 1 is the conductivity plot of the AB/PVDF film at different compositions. The conductivity increases with increasing AB content and peaks at 1:1.25 AB to PVDF.17 An increase in AB content beyond 1:1.25 resulted in cracked films and a significant decrease in the conductivity. This is due to the lack of PVDF binder needed to hold all of the AB particles together. When the composites are in contact with excess electrolyte, conductivities of the wet films are only a third as high as the conductivity of the dry films. The AB particles are separated with a thin layer of PVDF binder.18 It is well known that the PVDF swells...
The distance between the conductive AB particles is increased when the PVDF layer between the particles swells, resulting in the drop of electronic conductivity. The wetted condition is more representative of the electronic conductivity one might expect in a functioning cell. However, Fig. 1 shows that, even at AB/PVDF ratio of 1:5, the composite conductivity is still >0.1 S/cm, which is still far greater than the electronic conductivity of the active material and of the electrolyte, which has conductivity on the order of $10^{-2}$–$10^{-3}$ S/cm.\textsuperscript{20-22}

Among the compositions shown in Fig. 1, 1:2, 1:1.25, and 1:1 AB/PVDF were selected for further testing with active material. 1:1.25 gave the best electronic conductivity among all the AB/PVDF compositions; 1:2 and 1:1 have similar conductivity, but straddle the optimum. In the three electrode compositions tested, the conductive additive AB was fixed at 4 wt % and the PVDF and active material contents were varied in order to achieve the desired AB/PVDF ratios. Although the conductive additive is constant in all three compositions, the long-range electronic conductivity of the composite electrodes changed, as shown in Fig. 2. This trend is in agreement with the conductivity behavior of the AB/PVDF thin films (Fig. 1). In a noncalendared electrode film, 52% of volume is void space and 48% is occupied by AB/PVDF/LiNi\textsubscript{0.8}Co\textsubscript{0.15}Al\textsubscript{0.05}O\textsubscript{2}, as reported in the Experimental section. Considering the material densities and the PVDF and LiNi\textsubscript{0.8}Co\textsubscript{0.15}Al\textsubscript{0.05}O\textsubscript{2} contents, the volume ratio of the AB/PVDF is only ~10% of the total volume of the electrode, as labeled in Fig. 2. This 10% volume ratio of the AB/PVDF of the electrode agrees well with the 90% drop of long-range electronic conductivity of the composite films. The AB/PVDF composite is the major component to allow for conductivity of the electrode. A similar result of electronic conductivity drop is seen for composite films with electrolyte added. Despite the additional drop in conductivity of the composite electrodes, all three electrode compositions still maintain significantly higher electronic conductivities than the electronic conductivity of LiNi\textsubscript{0.8}Co\textsubscript{0.15}Al\textsubscript{0.05}O\textsubscript{2} or the ionic conductivity of the electrolyte.\textsuperscript{20-22}

**Morphologies of composites.**—SEM was used to help explain the AB/PVDF films’ surface morphology to their conductivity, as shown in Fig. 3. At low AB loading (Fig. 3A), a continuous polymer phase was clearly visible (white arrows) with aggregates of AB embedded in it. With increasing AB concentration (Fig. 3B and 3C), AB becomes more abundant on the surface with the retreat of the polymer phase. Although the 1:1 ratio of AB/PVDF appears uniform under visual examination, low magnification SEM images (Fig. 3C, inset) show extended micro cracks in the film. This loss of mechanical integrity is attributed to the decrease of conductivity with increasing AB content beyond the optimum electronic conductivity level at 1:1.25 AB/PVDF ratio.

In a working composite electrode, electrons are transported mostly through the AB/PVDF of the composite system and, therefore, the conductivity of this pathway is critical to the electrode performance. We therefore felt the need to study the morphology of this pathway more closely. AB/PVDF of 1:2, 1:1.25, and 1:1 ratios were studied. These three samples covered the binder rich, optimum conductivity, and AB-rich composition. As shown in the TEM images (Fig. 4), the acetylene black is not uniformly distributed in the binder. There are distinct phases that are either binder rich or AB aggregate rich. At higher binder contents, the AB forms extended three-dimensional networks to provide long-range conductivity while free polymer forms another phase within the AB network. At 1:2 composition, the TEM image (Fig. 4A) shows that pure PVDF phases exist that do not contribute to the composite long-range conductivity, and that extended AB agglomerate phase as current paths. There are very few visible regions of free polymer phases observable under TEM at a 1:1.25 AB/PVDF ratio and greater (Fig. 4B and 4C), because the PVDF is mostly associated with AB particles rather than form its own phases.\textsuperscript{23} As a reminder, electronic conductivity peaks at 1:1.25 and decreases at 1:1 AB/PVDF ratio. There appears to be a minimum requirement of polymer at 1:1.25 to tightly bind the particles together. The disappearing of free polymer phases with increasing AB ratio is due to the strong interaction between the polymer and AB particle surface. The polymer molecules can be adsorbed onto the AB surface either chemically or physically. With increasing AB content, the free polymer regions transform into mostly surface absorbed layers around the AB particles.\textsuperscript{5}

**Electrochemistry testing.**—Cathode laminates of varying AB/PVDF weight ratios of 1:2, 1:1.25, and 1:1 on aluminum substrates were tested in coin cells against lithium foil and MCMB counter electrodes. The AB content in all of the cells was held at 4%. The detailed cell compositions and configurations are listed in Table I. The porosity of the three electrodes was held constant at 35% in order to minimize the configuration effects of the cell performance.

![Figure 2. Long-range electronic conductivity of three LiNi\textsubscript{0.8}Co\textsubscript{0.15}Al\textsubscript{0.05}O\textsubscript{2} cathode films with constant 4% AB by weight. The “Vol.” labels indicate the volume ratios of the AB/PVDF composite to the overall electrode volume.](Image)

**Table I. Compositions and configurations of three LiNi\textsubscript{0.8}Co\textsubscript{0.15}Al\textsubscript{0.05}O\textsubscript{2} cathode electrodes.**

| AB: PVDF (w) | 1:2 | 1:1.25 | 1:1 |
| AB (w) | 4% | 4% | 4% |
| PVDF (w) | 8% | 5% | 5% |
| Active material (w) | 88% | 91% | 92% |
| Electrode thickness (\(\mu\text{m}\)) | 35 | 39 | 31 |
| Capacity (mAh) | 1.68 | 1.99 | 1.64 |
| Porosity | 35% | 35% | 35% |

![Figure 3. SEM surface images of the AB/PVDF composites: (A) AB:PVD = 1:2. Free polymer is seen on the surface of AB as pointed out by the arrows. (B) AB:PVD = 1:1.25. (C) AB:PVD = 1:1.](Image)
The capacity and thickness of the three electrodes were controlled to within 10% standard deviation in order to minimize the configuration effects to the cell performance. However, it should be noted that a small variation of either parameter cannot be entirely eliminated because active material content also changes a few percent due to the change of PVDF. Although there was only a 4% change of PVDF content, this brings a 50% change in the AB/PVDF ratios among three electrodes. All coin cell capacities agree well with the manufacturer suggested LiNi0.8Co0.15Al0.05O2 material capacity of 173 mAh/g during C/10 charge and discharge tests between 3 V and 4.1 V as shown in Table I. Figure 5 shows the rate performance of three lithium counter electrode cells. These cells are charged at C/10 rate and discharged at different rates. The discharge capacities of the cells are normalized to the C10 discharge capacity as shown in Table I. All three cells perform similarly at low to medium rate. However, the performances diverge at high rates. The electrode with the optimum electronic conductivity (AB/PVDF = 1:1.25) is not the best performing cell at high rates. The cell with the highest binder content (AB/PVDF = 1:2) gives the best capacity retention at greater than 5C. The cell with the lowest binder content (AB/PVDF = 1:1) performs the worst.

In order to better interpret these results, EIS was performed on all the cells at 40% DOD, as shown in Fig. 6. The major difference in the impedance data between the three cells is the interfacial resistance represented by the squashed semicircle in the high-frequency region of the spectrum. The width of the semicircle increases with decreasing binder content. Similar results were observed with coin cells made containing MCMB10-28 as the counter electrode, as shown in Fig. 7. The width of the semicircles in Fig. 6 and 7 each contain contributions from the interfacial impedance from the counter electrodes, with a smaller contribution coming from the graphite than that of the lithium. The increase in impedance with removal of binder is thus a major contributor to the cell impedance which in turn leads to a loss of capacity at high rates. HPPC tests were performed on three MCMB-based counter electrode coin cells, with the results plotted in Fig. 8. The area-specific impedance (ASI) data are in very good agreement with the EIS test, as the AB/PVDF = 1:2 composition gave the lowest ASI of the three cells across the entire depth of discharge (DOD) range, followed by 1:1.25, and then 1:1.

Figure 9 is a schematic of the cathode particle and its environment in the working electrode with lithium-ion transport and electron movement pathways identified. The open space is occupied by the electrolyte where lithium ions can move in and out of the active materials, while the black is the AB/PVDF electronic contact to the active materials. The schematic is not drawn to scale but is meant to aid the discussion of the possible contributions of the component during an electrochemical process. All three electrodes are designed to minimize the configuration contribution to the impedance. Since the porosities are controlled at 35%, the electrolyte mass-transfer rate within the electrode is very similar among all three compositions (Fig. 9A). The close matching of the capacities ensures very similar active material surface areas among all three electrodes.
There are two major changing factors among the three electrodes. The long-range matrix electronic conductivities of the electrodes are in the order of 1:1.25 > 1:1 > 1:2. Should the matrix conductivity be the limiting factor (Fig. 9B) for all three electrodes, the power performance starting from the best would be on the order of 1:1.25 > 1:1 > 1:2. PVDF is viewed as a nonconductive material in the electrode. Increasing its amount could exert a lithium-ion blocking effect both in the electrolyte and at the active material interface, which might slow down the lithium-ion transfer in the electrolyte or at the interface (Fig. 9A and 9C). Should this be the scenario, the power performance starting from the best would be 1:1 > 1:1.25 > 1:2. Neither of the above hypotheses is correct. Instead, the electrodes with increasing binder content perform better as a result of the improved charge-transfer kinetics. One possibility is the variation of the electronic conductivity (Fig. 9D) between the active material particles and the AB/PVDF composite, which can affect the lithium-ion transfer at the interface. Figure 10 shows a schematic of the active material particle in combination with the TEM image of the AB/PVDF composites. This schematic is not drawn to scale but to illustrate the possible mechanism of the critical role of the binder in designing a cell for power performance. The existing of pure polymer phase in 1:2 (Fig. 10A) may serve a critical function to provide and maintain better mechanical contact between the active material and AB conductive pathways rather than slowing down lithium-ion transfer at the interface. Intimate contact between the AB and the active materials allows effective local electronic charge injection therefore facilitating lithium-ion transfer at the interface. At low binder loading, the AB tends to move away from the active material to form self-assembled agglomerates due to the flocculation phenomenon; thus AB microscale structures play a critical role in interfacial impedance.

Conclusion

The long-range electronic conductivity in a composite electrode is almost exclusively provided by the AB/PVDF matrix. A wide range of compositions of AB/PVDF ratios tend to satisfy the long-range electronic conductivity requirement of lithium-ion cathodes. This long-range electronic conductivity does not play an important factor for high rate performance as much as the interfacial resistance does. Our research indicates that the ratio of carbon conductive additive to binder ratio is a critical parameter in optimizing the interfacial resistance, with higher binder contents being more beneficial. Thus, the PVDF binders play a significant role in that it not only helps maintain electrode integrity, it also provides intimate contact between the conductive additive and the active material particles resulting in high, localized electronic conductivity at the active material interface thus decreasing interfacial impedance.
Acknowledgment

This research was funded by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies of the U.S. Department of Energy under contract no. DE-AC03-76SF00098.

Lawrence Berkeley National Laboratory assisted in meeting the publication costs of this article.

References