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

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Lithium ion rechargeable batteries are a prime candidate for electric vehicle (EV) and hybrid electric vehicle (HEV) applications due to their high energy capacity and light weight. These applications, especially HEV application, require low internal impedance for superb high rate charge and discharge performance. We focus on improving the electronic conductivity of the porous composite electrodes of the lithium ion cells. At the cathode side, conductive pathways are formed within the acetylene black and polyvinylidene fluoride (PVDF) region to sustain the electronic current flow. The overall electrode conductivity and mechanical integrity are directly related to the acetylene black nano-particle and PVDF binder composite system. A two-step mixing process was adopted to make the composite cathode electrode. First step is to form a conductive glue system containing PVDF and dispersed acetylene black in NMP. The second step is to mix an active material into the conductive glue.

In order to understand the conductive behavior of the acetylene black and PVDF composite system, different weight ratios of acetylene black are dispersed in PVDF NMP solution, and cast into thin films. The film compositions extend from 0.1:1 to 1:1 acetylene black to PVDF, which are representative of those found in commercial cells. The films show cracks beyond the 1:1 ratio, meaning that the mixture could not effectively maintain itself into a film. Using conductive glue beyond 1:1 ratio will result in a mechanically weak electrode. The conductivity of the films was measured using the four-probe technique. The dry film conductivity was measured after the film was dried in a vacuum oven. Later, the film was wetted with electrolyte solvent and its conductivity was measured again. Figure 1 shows the conductivity increasing with the acetylene black ratio and peaks at 0.8:1 acetylene black to PVDF. Further increases in acetylene black content decrease the conductivity significantly. The conductivity of solvent wet films follows the trend of the dry films, but with only of a third of the conductivity of the corresponding dry films.

The acetylene black and PVDF composite film is nano-scale inhomogeneous as show in the Transmission electron microscope (TEM) image. (Figure 2, a) There are two distinct regions, an acetylene black rich region and a polymer rich region. The acetylene black rich region is coated with PVDF polymer providing mechanical integrity. The branch structure of the acetylene black is clearly preserved from the original acetylene black powder. (Figure 2, b) PVDF coatings integrate these conductive branches to form continuous electronic pathways.

Figure 3 shows the actual electrode conductivity made from the conductive glue and cathode material. In this case, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ was used as active material. The acetylene black content was fixed at 4% by weight in the all 3 electrodes, but the amount of PVDF binder was varied to achieve 0.5:1, 0.8:1 and 1:1 acetylene black to PVDF. The conductivity changes according to the binder content at a constant acetylene black level in three electrodes. This trend is in agreement with the conductivity behavior of the PVDF and acetylene black composite thin films as shown in Figure 1.

ACKNOWLEDGEMENTS

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.

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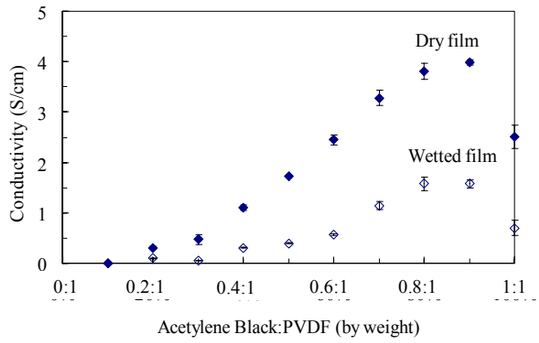

Figure 1. Conductivity changing with composite film composition.

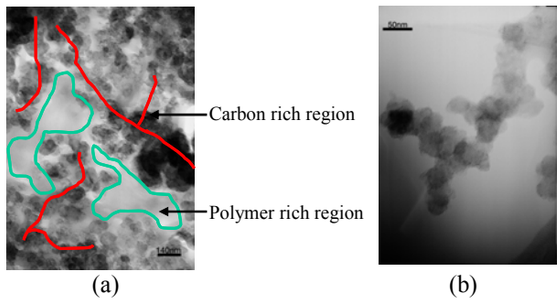

Figure 2. (a) A cross-section of 0.5:1 acetylene black and PVDF composite film viewed under TEM. (b) Pure acetylene black powder forms branches.

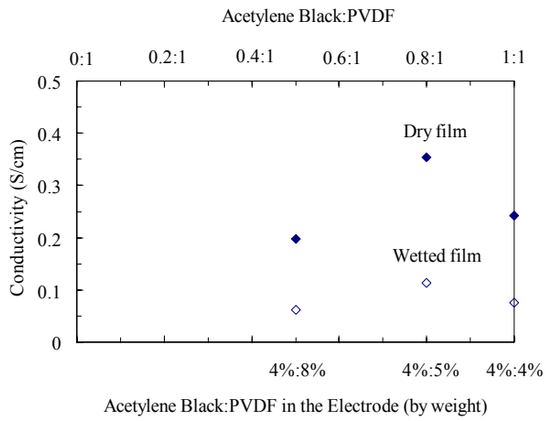

Figure 3. Conductivity of 3 $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ based cathodes at the same 4% acetylene black additive level.