

Improving the Cycling Life of a Li-ion Battery

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Introduction:

Magnetite (Fe_3O_4) is a high capacity material, used to improve the battery life within a Li-ion battery. Although high capacity materials are known to improve battery life, it is common for volume expansion to occur during the Li insertion process; therefore, disrupting the charge transfer within the battery. In order to provide alternative charge pathways, poly[3-(potassium-4-butanoate)thiophene] (PPBT) was used as a binder within the electrode. Also, polyethylene glycol (PEG) was used as a coating for Fe_3O_4 in order to reduce aggregate size. Altogether, these components were used to increase electron and ion transport within the battery. In this study, different derivatives of PPBT were tested to see their effect on the overall battery performance.

Using ion exchange resin, the potassium ion was replaced with ammonium, hydrogen, or potassium again in order to understand the ions' interactions within the system and how they affect the battery. X-ray Photoelectron Spectroscopy (XPS) is used to confirm the ion exchange for P-K-BT, P-NH₄-BT, and P-H-BT. Electrodes are fabricated from a mixture of PEG- Fe_3O_4 , a polymer binder, and carbon black. Scanning electron microscopy (SEM) was used to determine the morphology of the electrode. All electrodes were well-dispersed and their dispersion was comparable to a PPBT electrode.

Experimental Procedure:

The magnetite was first coated with PEG through ultra-sonication. 0.5 g of Fe_3O_4 was mixed with 5 g of DI water. 2 mL of PEG was added to the solution, which was then sonicated for 30 s. This was done four times so that 8 mL of PEG was added to coat the Fe_3O_4 . The PEG- Fe_3O_4 powders were washed with acetone and then separated by centrifuge. This was done three times. Thermogravimetric analysis (TGA) shows that the average coating of Fe_3O_4 was 9.74% by weight.

To produce P-H-BT, 5g of ion-exchange resin was added to a solution of 80 mg of PPBT in 10 mL of DI water. The ion exchange resin removes the potassium ion and replaces it with the hydrogen ion. To produce P-K-BT or P-NH₄-BT, 1M KOH or 1M NH₄OH was added as well. P-K-BT was studied to see if it will perform differently to PPBT, although they should have the same chemical composition. P-H-BT was studied since it is the intermediate in the ion-exchange step. If the electrode containing P-H-BT performs well, then there may be no need to add a different ion. P-NH₄-BT is studied as a substitute to PPBT.

XPS was used to determine if the ion exchange was successful. The survey scan for P-NH₄-BT showed that NH₄, C, O, and S were present, while revealing that no K was present in the sample. K, C, O and S was present in the P-K-BT survey scan. C, O, and S were present in

the P-H-BT sample, and no K was present. H cannot be detected using XPS, but since there is no K present, it can be assumed that the ion is H.

Slurries of the electrodes were prepared by mixing a 71.4:14.3:14.3 ratio of PEG-Fe₃O₄, Carbon Super P, and PPBT or one of its ion derivatives. The electrodes were fabricated by blade-coating the slurry onto a sheet of copper foil. Electrodes are set out to air dry for 1 h and then set to dry in a vacuum oven at 110 °C for 12 h.

Results and Discussion:

Carbons scans from XPS showed that the slurries containing PPBT and P-K-BT had four carbon peaks rather than the just two carbon peaks from the C-O bond and carboxylate group. These satellite peaks are predicted to indicate π - π stacking, which may improve the charge transport within the system. Iron scans from XPS indicate three peaks. According to previous studies, the second peak is only present when the PEG-Fe₃O₄ is mixed with PPBT or one of its ion-derivatives, and shows interactions between the magnetite and polymer binder. It is predicted that this peak indicates an iron-carboxylate group.

SEM images showed the morphology of each electrode. All electrodes had similar dispersion, and show no significant change from the PPBT control electrode. Dynamic Light Scattering (DLS) was then used to obtain the particle size of the polymer binders. P-NH₄-BT had an average aggregate size of 224.3 nm \pm 77.7 nm. P-K-BT had two average aggregate sizes: 280.8 nm \pm 206.4 nm and 17.62 nm \pm 7.21 nm. The 280.8 nm particle was the more present size by 94.2%. It is predicted that P-K-BT is less soluble in water based on the standard deviation. DLS was unable to be done on P-H-BT since it is not very soluble in water. It is predicted that smaller particle sizes increase charge transport within the system due to increased surface area.

Conclusion and Future Work:

XPS shows that the ion exchanges for all polymer binders were successful. Satellite peaks from the carbon scan indicate π - π stacking. These new interactions may improve the electronic performance of the system. Iron scans show a satellite peak that indicates interactions between the magnetite and the polymer binder which may also improve electronic performance. The morphology of each electrode is similar, but P-NH₄-BT generally has smaller aggregate sizes than P-K-BT, which may lead to better charge transport within the system. In the future, cycle life tests, rate capability tests, and conductivity tests will be done in order to characterize the electronic performance of each electrode.

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