Effect of Binders on the Surface Morphology and Adhesion Strength in the Anodes of Lithium Ion Batteries

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In the rocking-chair rechargeable lithium ion batteries, anodes predominantly consist of graphite bound by polymeric binders like poly(vinylidene fluoride) (PVDF). Polymeric binder, which is necessary to provide sufficient mechanical strength to the electrodes, can be subjected to electrochemical reaction. Reactions of binder with the lithium ion of lithiated carbon begin above 300°C,[1] so a direct reaction is not considered important during processing and operation. However, there is an influence of the binder on the reaction between lithium ions and electrolyte, which takes place at the carbon surface. It is known that the kind and amount of binders affect the electrochemical efficiency[2], and chemistry of the carbon surface is important to SEI formation.[2,3] However, the interaction and interface between graphite and binders have not been studied extensively. In this report, we have studied the effect of binders on the surface morphology of binders and adhesion strength by using different molecular weight and functionality. Also we have investigated the solvent effect on the morphology of binders.

We used 8 kinds of carbon materials: synthetic graphite MV2 (Mitsubishi Chemical Corp., Japan), SFG15, SFG44, SFG75 (Timcal Co. Ltd., Switzerland), KS6, KS15 (Timcal Co. Ltd., Switzerland), and mesocarbon microbeads (MCMB-, Oosaka Gas Chem., Japan); MBC-N (Mitsubishi Chemical Corp., Japan) as amorphous carbon material. Anodes were prepared by mixing carbon slurries that contained each of carbon materials, 1-metyl-2-pyrrolidinone (NMP, anhydrous, Aldrich) as a solvent and 10 wt% solution of poly(vinylidene fluoride) (PVDF) binder (Mw=350k, Kureha, KF#1300) in the same solvent. To investigate the effect of molecular weight and functionality, we used a PVDF with molecular weight of 500k (Atofina, Kynar 301F) and a modified PVDF with –COOH and –OH (Atofina, MKB 212A). And we used alternative solvents such as N,N-dimethylacetamide (DMA) and N,N-dimethylformamide(DMF). The solid concentration of slurries was 40 wt%. We spread the slurries using doctor-blade method on a sheet of copper foil and dried them in an oven at 83 ºC for 1 hour to form 95/5 wt% of graphite/PVDF composite anodes

We performed Scanning Electron Microscopy (SEM), Electron Probe X-ray MciroAnalysis (EPMA), and Energy Dispersive Spectroscopy (EDS) to investigate the distribution of polymeric binders on the graphite surface. We used a scrape adhesion tester (ASTM D-2197) to investigate the adhesion strength to anodes.

Data from EDS and EPMA show that low viscosity materials before doctor-blading turn out to have more inhomogeneous distribution of PVDF on the surface of carbon after curing than those with high viscosity. And polymeric binders inhomogeneously reside at the edge and grain boundaries of graphite rather than in the center. PVDF with higher molecular weight and modified functionality shows an improved homogeneity of PVDF distribution and different solvents used in mixing appear to affect the degree of homogeneity.

Controlling PVDF distribution that can affect SEI formation and the effect of binders on the adhesion strength will be presented.

References

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