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EFFECT OF CONDUCTING POLYMER BINDER ON THE ELECTROCHEMICAL PERFORMANCE OF ELECTRODE MATERIALS FOR LITHIUM-ION BATTERIES

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The electrodes of Li-ion batteries usually consist of several components such as rechargeable material grains, conducting and binding components. Due to the insufficient conductivity of most inorganic rechargeable compounds used as active grains in electrodes of lithium ion batteries, a conductive additive, such as carbon black or other carbon materials, is necessary to increase the electrical conductivity. Nanostructuring and carbon coating of active grains are considered as very effective approaches for the increase of material conductivity. Also a polymeric binder is required to bind active grains and other additives together in one electrode material with desirable mechanical properties and adhesion to current collector. PVDF inert binder, which is commonly used for fabrication of commercial Li-ion batteries, provides strong adhesion between battery components and current collector, but its serious drawbacks are electrically insulating properties and the necessity to use the toxic solvent NMP for electrode procession. Besides, since both the binder and carbon conductive additives are electrochemically inactive and their total content may reach 10-15% of total mass of electrodes, it is desirable to minimize their amount.

The search of new conductive and binder components and their combinations for electrode materials, allowing to increase the electronic and ionic conductivity of host media, as well as integrity of material and stability, is a current trend. Among the proposed alternative polymer materials are monocomponent binders based on PEDOT:PSS or CMC polymers alone or in combination with PVDF, some of them turned out effective for a number of materials [1,2]. Recently, we proposed a novel composition of combined conductive polymer binder, which possesses both functions of strong binder and electrical conductor [3-5]. This conductive binder is based on the proper combination of PEDOT:PSS and CMC polymers.

The surface modification of rechargeable material grains with PEDOT:PSS/CMC provides both an increase in ionic and electronic conductivity as well as protection of active material particles from interaction with the solvent and suppression of material dissolution, which deserves special attention for such material as LiMn_2O_4 . Another positive impact of conductive polymer binder could be related to the more elastic electrical contact between the grains of the electroactive material. During intercalation of lithium, when expansion and contraction of the lattice occurs, whereby the active material may lose the contact with carbon additives, but in case of elastic binder maintains the contact. This should improve the cycling stability of the electrode. Finally, the use of water-soluble, conductive polymers as environmentally friendly binder for electrode fabrication, leads to more safety industrial processing technique and batteries.

We have investigated the effect of conducting polymer binder on the performance of different composite electrode materials. The effect of conductive binder was tested for the series of compositions of cathode (LiFePO_4 (LFP), $\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$ (LFMP) and LiMn_2O_4 (LMO)) and anode ($\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO)) materials with different amount of PEDOT:PSS and CMC/PEDOT:PSS. The ratios of binder, carbon and polymer conductive additives were optimized in the electrode multicomponent mixture to achieve the maximal fraction of active material and specific capacitance. The morphology and structure of prepared composites were characterized by XRD and SEM, surface chemical composition of electrode materials was investigated by XPS analysis.

The electrochemical properties of the prepared electrodes were studied by cyclic voltammetry, galvanostatic charge-discharge and EIS in CR2032 type coin battery cells. For all cases of employment of conductive binder we have observed the improved electrochemical responses in terms of reversibility of electrode processes and lower internal resistance of materials (smaller difference between potentials of cathodic and anodic peaks), increased specific capacitances.

Galvanostatic charge-discharge tests were performed at different current rates from 0.2 C to 20 C at room temperature ($20 \pm 2^\circ\text{C}$). It was found that in all cases the employment of polymer binder PEDOT:PSS/CMC along with small amount of carbon black in the active electrode material improved the specific capacity of electrodes compared to the conventional PVDF bound electrodes for about 10-20%. The most effective impact of the replacement of PVDF binder by conductive binder was observed for the LFP and LTO materials, whereas the manganese containing LFMP and LMO materials show less

significant increase of the specific capacity. It may be due to higher intrinsic conductivity of these materials. The long-term cycling stability tests showed the satisfactory maintenance of specific capacities at least for 200-300 cycles.

It was also shown that the rate capability of electrodes can be significantly improved by the optimized composition of conductive binder. This can be due to the improved overall conductivity of mixed polymeric binder. To support these conclusions the additional measurements of the electronic and ionic conductivity of the composite electrodes were performed by using four-probe method and EIS measurements.

A comparative analysis of the kinetic parameters of the system studied was performed by systematic EIS measurements in the battery cells. The obtained kinetic parameters (interfacial resistances, apparent Li^+ diffusion coefficients) allow to reveal the role of different components in electrochemical performance of cathode material. The obtained parameters of electrochemical impedance were compared for different compositions of electrodes. It was found that two main parameters suffer most drastic changes: the decrease of interfacial charge transfer resistance R_{ct} and increase of diffusion coefficient D_{eff} at the transition from conventional composition of materials to modified by conductive binder. It was observed as a trend for all investigated active materials. Detailed analysis of electrochemical performance of different electrodes will be discussed.

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