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Aqueous processed Li-ion battery electrodes with hydrolyzed polyacrylonitrile binder

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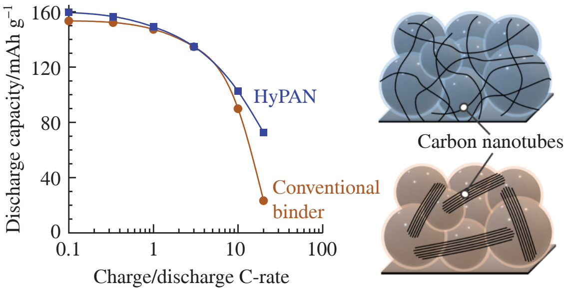
We have developed $LiFePO_4$-based battery electrodes using carbon nanotubes as the electrically conductive component and hydrolyzed polyacrylonitrile (HyPAN) as the polymer binder. The developed binder allows the electrodes to be manufactured environmentally friendly from a water-based slurry. Moreover, HyPAN provides a more homogeneous distribution of carbon nanotubes inside the electrode and better rate performance compared to popular binders.



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In recent years, there has been a significant increase in the demand for lithium-ion batteries for electric vehicles and energy storage systems. Optimizing the composition of battery electrodes to meet practical requirements for energy density and sustainability is a challenging task. One of the main challenges is the development of effective polymer binders that ensure the mechanical integrity of the electrodes.[1–3] Much attention is paid to replacing the commonly used polyvinylidene fluoride (PVDF) with water-soluble binders, which allow the electrodes to be manufactured more safely and cheaply without the use of toxic and flammable organic solvents.[4–6] The production of electrodes from water-based slurries eliminates the need for a solvent recovery system.[4] In addition, this technology provides a faster and less energy-consuming drying process,[7] as well as a simplified method for recycling the electrodes.[8]

The combination of sodium carboxymethyl cellulose (CMC) and styrene–butadiene rubber (SBR) is the most commonly used water-soluble binder for electrodes.[9] However, CMC/SBR exhibits limited oxidative stability[10,11] and requires a complicated sequential mixing procedure.[12] Therefore, the development of new water-based binders, especially single-component ones, remains a significant challenge. An ideal binder should be able to ensure good dispersion quality of the electrode slurry and prevent aggregation of electrode components, such as carbon nanotubes, which are used as a promising electrically conductive additive for high-energy-density electrodes.[13,14] Well-dispersed carbon nanotubes provide improved electrochemical performance of electrodes compared to agglomerated ones.[15–18]

In this work, we present hydrolyzed polyacrylonitrile (HyPAN) as a novel single-component binder for aqueous processed Li-ion battery electrodes. HyPAN is a water-soluble and commercially available copolymer composed of acrylic acid and acrylamide units.[19] We demonstrated the ability of HyPAN to stabilize single-walled carbon nanotube (SWCNT) dispersion in electrode slurry and improve the homogeneity and electrochemical performance of the electrodes compared to traditional PVDF and CMC/SBR binders.

Cyclic voltammetry experiments in the potential range of 2.0–4.5 V *vs.* Li/Li^+ showed that HyPAN and PVDF exhibit better electrochemical stability than CMC/SBR (Figure S1, see Online Supplementary Materials). This electrochemical window covers the operating range of positive battery electrodes based on $LiFePO_4$ and Mn-substituted $LiFe_{1-x}Mn_xPO_4$ materials.[20] In contrast, the CMC/SBR binder is unstable at potentials above 4.0 V (see Figure S1) due to oxidation of the C=C bonds of SBR.[10,11] For this reason, we limited the upper cut-off potential by 4.0 V for further electrochemical experiments.

Before preparing the battery electrodes, we investigated the ability of HyPAN to stabilize aqueous dispersions of SWCNTs. SWCNTs demonstrated poor dispersibility in HyPAN solution at pH 7. When the pH was decreased to 5, the aggregation stability of SWCNTs in HyPAN solutions increased significantly and reached 1.04 mg ml^{-1} (dispersion yield of 98.7% with respect to the total amount of added SWCNTs), as measured by spectrophotometry (Figure S3). The resulting dispersions were stable after centrifugation at 10 000 rpm without phase separation.

The aqueous dispersions of SWCNTs prepared at pH 5 were used to develop $LiFePO_4$-based battery electrodes with the $LiFePO_4$/HyPAN/SWCNT weight ratio of 95 : 4.75 : 0.25, which was based on the results of our previous study.[13] In the process, the composite electrodes were deposited from the slurries as described in Online Supplementary Materials. It is worth noting that pH 5 is well within the stability ranges of $LiFePO_4$ particles[21] and aluminum current collector,[22] thereby confirming the applicability of the developed slurries for the fabrication of $LiFePO_4$-based battery electrodes. Electrodes with commonly used PVDF and CMC/SBR binders were prepared with the same composition using NMP and water as dispersion media, respectively.

Figure 1 shows the SEM micrographs of the electrodes fabricated using different binders. The electrodes prepared using PVDF and CMC/SBR binders contain thick SWCNT bundles with a maximum diameter of 100 and 40 nm, respectively, which are located on the surface of $LiFePO_4$ microparticles (see Figure 1). In both cases, the SWCNT bundles are unevenly distributed, and

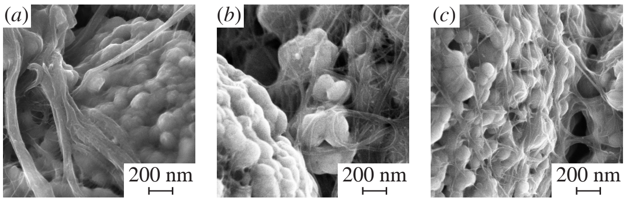

Figure 1 SEM micrographs of the surfaces of $LiFePO_4$-based electrodes prepared using different polymer binders: (*a*) PVDF, (*b*) CMC/SBR and (*c*) HyPAN.

a significant area of the $LiFePO_4$ surface is not in contact with the SWCNTs (see Figure 1). In contrast, the electrode fabricated using HyPAN contains finely dispersed SWCNT bundles of 5–15 nm thickness, forming a dense and uniform network wrapping the surface of the $LiFePO_4$ particles and connecting them together (see Figure 1). This is consistent with the good stability of SWCNT dispersion in HyPAN solution at pH 5 (Figure S2).

PVDF has poor dispersing ability and prevents SWCNT agglomeration mainly due to the increase in slurry viscosity.[16] CMC has rather rigid backbone chains with a high persistent length (*ca.* 16 nm)[23] and therefore tends to form thick adsorption layers, which can be an obstacle in debundling of SWCNTs. In contrast, HyPAN has flexible chains with a more coiled conformation that are easily adsorbed on the surface of SWCNTs, thereby preventing the agglomeration of individual SWCNTs into bundles *via* van der Waals interactions.

Figure 2(*a*) compares the rate capability of $LiFePO_4$-based electrodes prepared with different binders that have been investigated in standard lithium half-cells. At a low charge/discharge rate of C/10, the electrodes demonstrate the same capacity of *ca.* 155–160 mAh g^{-1} [see Figure 2(*a*)], which is close to the theoretical value of $LiFePO_4$ (170 mAh g^{-1}). At higher rates, the HyPAN-containing electrode exhibits the best performance, still delivering 60 mAh g^{-1} at a rate of 20C. We believe that this is due to the efficient charge transport resulting from the homogeneous distribution of SWCNTs across the electrode. The poorer rate capability of the electrodes with PVDF and CMC/SBR binders (23 and 27 mAh g^{-1} at 20C, respectively) may be due to the stronger agglomeration of SWCNTs in these electrodes (see Figure 1), which leads to a higher potential gradient, incomplete utilization of the active material capacity and poorer Li^+ ion (de)intercalation kinetics.

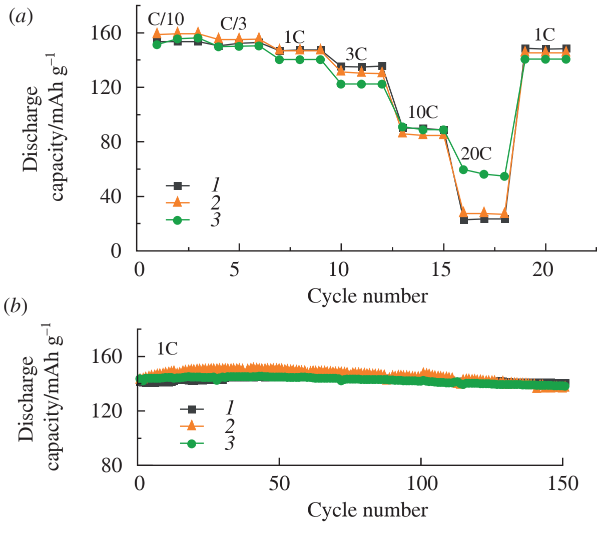

Figure 2 (*a*) Rate performance and (*b*) cycle performance of composite electrodes prepared using different polymer binders: (*1*) PVDF, (*2*) CMC/SBR and (*3*) HyPAN.

The electrodes fabricated using both HyPAN and PVDF demonstrate stable performance during 150 charge/discharge cycles, retaining more than 97% of the initial capacity, while the CMC/SBR electrode exhibits a capacity loss of 4.5% [Figure 2(*b*)], which can be attributed to the inferior electrochemical (see Figure S1) and mechanical properties of the CMC/SBR binder.

In summary, we have developed aqueous-processed high-energy-density battery electrodes with commercial HyPAN combined with SWCNTs as a conductive component. When HyPAN is partially protonated, it prevents the tendency of SWCNTs to agglomerate in aqueous media, thereby ensuring the formation of homogeneous aqueous electrode slurries. This results in a uniform distribution of SWCNTs within the composite electrodes and a better contact between SWCNTs and active $LiFePO_4$ particles. The uniform distribution of SWCNTs results in improved cycling stability and good electrochemical performance of the electrodes at a high charge/discharge rate (20C), which is significantly superior to traditional PVDF and CMC/SBR binders.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7638.

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