Encapsulating silica into PAA/FGODs/PPy for conductive hydrogels

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Abstract. Hydrogels crosslinked by polyacrylic acid (PAA) own good mechanical properties and strong tensile strength, can remain stable during long-term cycling and do not fail due to fracture. As a model of electrode active materials, nano silica was encapsulated into a composite hydrogel of functional graphene quantum dots (FGQDs), polypyrrole (PPy) and PAA to obtain a FGQDs/PAA/Si/PPy hydrogel. The nanostructure and conductivity of FGQDs/PAA/Si/PPy hydrogels were analysed, and the hydrogels were promising as aqueous binders.

1. Introduction

Binder is an important part of the electrode material of lithium-ion battery. By bonding the active materials with conductive agents as well as the current collector, the choice of binder has large influence on the quality and performance of lithium-ion battery. [1-3] Aqueous binder has the advantages of organic solvent free, environment-friendly, cheap, convenient and safe, the functional groups in the structure of binder can bond with the electrode materials, so as to improve the bonding performance. [4-7] Thus the research on aqueous binders is a promising future trend of lithium-ion battery binder.

To increase the conductivity of aqueous binders, it is necessary to add conductive agents to realize the charge transfer inside the electrode. [8] However, these charge transfer paths will be damaged due to the volume shrinkage of the active substance and the displacement of the conductive agent during the charge discharge cycle of the electrode, causing the loss of the charge transfer path and the decreasing of the bonding performance. Considering these, it is preferred if the binder itself has good conductivity. In this way, the binder can form electron and ion transmission channels, establish a good conductive network and reduce the mass fraction of inert components, thus enhance both the energy density and the power density of the electrode. Therefore, enhancing or endowing the aqueous binders with conductivity has become a new hot spot in recent years.

As an aqueous binder, polyacrylic acid (PAA) offers good adhesion to the electrode materials, ensures the close contact of granular materials, promotes the rapid transfer of charge, inhibits the volume change of LiFePO4 material during charging and discharging, and improves the adhesion between active materials and metal collector. [9] Hydrogels crosslinked by PAA own good mechanical properties and strong tensile strength, can remain stable during long-term cycling and do not fail due to fracture. [10] In our previous study, a functional graphene quantum dots (FGQDs) and polypyrrole...
(PPy) incorporated PAA hydrogel (FGQDs/PAA/PPy) was synthesized, the FGQDs and PPy significantly improve the conductivity of the PAA binder.[11] Herein, the morphology and conductivity of the silica encapsulated FGQDs/PAA/PPy hydrogels were studied to further indicate the potential performances of FGQDs/PAA/Si/PPy hydrogels as aqueous binder.

2. Experimental

2.1. Materials
Acrylic acid, citric acid, pyrrole, ammonium persulfate (APS) and N, N-methylene bisacrylamide (MBA) were bought from Sinopharm Chemical Reagent Co., Ltd. Acrylic acid was distilled under vacuum condition before use. Nano silica powder (diameter of 50 nm) was bought from MTI Corporation.

2.2. Characterization
Morphology was collected on an optical microscope (Olympus BX53, Japan) and a Verios 460 SEM. Electrical property was measured by a Gamry Reference 3000 Potentiostat/Galvanostat/ZRA instrument.

2.3. Preparation of FGQDs
FGQDs were prepared by the pyrolysis of citric acid together with MBA. Generally, 4.2 g of citric acid and 0.62 g of MBA were mixed in 20 mL of H2O, incubated at 200 °C for 3.5 h, cooled down, filtered through a 220 μm membrane, and dialyzed in H2O for 2 days to get the FGQDs.

2.4. Preparation of FGQDs/PAA/Si hydrogels
FGQDs/PAA/Si hydrogels were synthesized by the polymerization of acrylic acid with the presence of FGQDs, nano silica, APS and MBA. Generally, 4 mL of acrylic acid, 15 mL of H2O, 30 mg of APS, 30 mg of MBA and 100 mg of FGQDs were mixed, then nano silica (5, 10, 20, 50 mg, ratio of FGQDs to Si =20, 10, 5, 2) was added. The mixture was kept at 70 °C for 12 h to get the FGQDs/PAA/Si hydrogels.

2.5. Preparation of FGQDs/PAA/Si/PPy hydrogels
FGQDs/PAA/Si hydrogels were vibrated in H2O until reaching swelling equilibrium. Then, the hydrogels were taken out and put into the aqueous solution of pyrrole (0.7-14.4 mM, avoiding light) for 24 h. After which, APS (pyrrole : APS = 1:1) and HCl (final concentration of 1 M) were added, and shake for 6 h to get the FGQDs/PAA/Si/PPy hydrogels. The hydrogels were vibrated in H2O for 48 h to reach swelling equilibrium.

3. Results and Discussion
The adding of FGQDs that were prepared by citric acid pyrolysis to the binder of the electrode can significantly improve the mechanical strength, elastic modulus and conductivity of the binder, and further enhance the electrochemical performances of the electrodes.[12-14] Using crosslinked PAA as matrixes, FGQDs as a cross-linker, and polypyrrole as an electro conducting component, composite hydrogels of FGQDs/PAA/PPy showed a high conductivity of 0.29 S/m, highly promised as a conducting element.[11] As a frequently-used anode material of lithium battery, nano silica has advantages of good dispersion, good electrochemistry, large specific surface area, high surface activity, and low bulk density. In this paper, nano silica was applied as a model of electrode active materials to incorporate into the hydrogels of FGQDs/PAA/PPy. The nano silica was dispersed in water containing acrylic acid monomer and FGQDs, then hybrid into the three-dimensional network structure of FGQDs/PAA/PPy hydrogels.
Fig. 1 Micrographs of (A) FGQDs/PAA, (B) FGQDs/PAA/Si, ratio of FGQDs to Si = 20, (C) FGQDs/PAA/Si, ratio of FGQDs to Si = 5 (D) FGQDs/PAA/Si/PPy (0.7 mM of pyrrole), (E) FGQDs/PAA/Si/PPy (2.9 mM of pyrrole), and (F) FGQDs/PAA/Si/PPy (14.4 mM of pyrrole) hydrogels.

Fig. 1A-1C showed the micrographs of FGQDs/PAA, and FGQDs/PAA/Si with different content of nano silica, which all exhibited porous structure. The nano silica dispersed evenly in the hydrogel matrixes. The induction of PPy produced a deepening color (Fig. 1D-1F), both the silica and PPy changed not the porous structure of the hydrogels. The SEM images showed a similar result. FGQDs/PAA showed a smooth surface (Fig. 2A), FGQDs/PAA/Si showed granular roughness on the surface (Fig. 2B & 2C), while the polymerization of pyrrole led to a further decoration of PPy particles.

Fig. 2 SEM images of (A) FGQDs/PAA, (B) FGQDs/PAA/Si, ratio of FGQDs to Si = 20, (C) FGQDs/PAA/Si, ratio of FGQDs to Si = 5 (D) FGQDs/PAA/Si/PPy (0.7 mM of pyrrole), (E) FGQDs/PAA/Si/PPy (2.9 mM of pyrrole), and (F) FGQDs/PAA/Si/PPy (14.4 mM of pyrrole) hydrogels.

Fig. 3 Conductivity of the FGQDs/PAA/Si hydrogels with different ratio of FGQDs to nano silica.
FGQDs/PAA hydrogels own ionic conductive three-dimensional network structure. The FGQDs/PAA hydrogels exhibited a conductivity of ~0.034 S/m. Nano silica did not alter the conductivity of the hydrogels obviously. For example, with 5-20 mg nano silica in the system, the conductivity stayed at ~0.035 S/m (Fig. 3).

![Fig. 4 Conductivity of the FGQDs/PAA/Si/PPy hydrogels that prepared in different concentrations of pyrrole (Py).](image)

The introduction of PPy highly increased the conductivity of the composite hydrogel. Pyrrole monomer can incorporate into the network of FGQDs/PAA/Si hydrogels and adsorb on the functional groups of FGQDs. After the polymerization, pyrrole monomer polymerized in situ inside the networks to achieve the interpenetration and filling of the conductive PPy. As shown in Fig. 4, the FGQDs/PAA/Si/PPy hydrogels synthesized with different amount of pyrrole produced a conductivity of 0.03-0.316 S/m with a highest conductivity of 0.316 S/m, comparable to a lot of PAA-based hydrogels, and promising as aqueous binders.

4. Conclusion
The encapsulating of nano silica did not alter the conductivity of FGQDs/PAA hydrogels. PPy endowed the composite hydrogels with high conductivity, the FGQDs/PAA/Si/PPy hydrogels exhibited a high conductivity of 0.316 S/m, promising as aqueous binders.

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