Sodium Alginate Binders for Bivalency Aqueous Batteries

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ABSTRACT: Environmental friendly sodium alginate (SA) cannot be used as a binder in aqueous batteries due to its high solubility in water. A water-insoluble polyvinylidene difluoride (PVDF) binder has been widely applied for an aqueous battery, in which the toxic and expensive organic solvent of *N*-methy-2-pyrrolidone (NMP) is required during the coating process. Herein, we report that the water-soluble SA can be utilized as a binder in aqueous Zn batteries because SA could cross-link with the Zn²⁺ ion to form a waterinsoluble and mechanically super strong binder for electrodes. Aqueous ZnllLiFePO₄ cells are assembled to demonstrate the performance of the SA binder for LiFePO₄ cathodes. Due to the high adhesion strength of cross-linked Zn-SA, LiFePO₄ with the SA binder displays a high capacity retention of 93.7% with a high Coulombic efficiency of nearly 100% after 100 cycles at a 0.2 C rate,



while the capacity of LiFePO₄ with the PVDF binder quickly decays to 84.7% after 100 cycles at 0.2 C. In addition, the LiFePO₄ cathode with the SA binder also has smaller redox polarization, faster ion diffusion rate, and more favorable electrochemical kinetics than that with the PVDF binder.

KEYWORDS: sodium alginate, water-soluble binder, bivalency Zn-ion electrolyte, aqueous battery, adhesion strength

1. INTRODUCTION

Binders play a critical role in enhancing the mechanical strength of electrodes and improving the electrochemical performance of a cell.^{1–3} Polyvinylidene difluoride (PVDF) is one of the most popular binders for aqueous batteries due to its water insolubility, excellent electrochemical stability, and adhesion properties.^{4,5} However, the toxic and expensive organic solvent N-methy-2-pyrrolidone (NMP) has to be used in preparing the slurry. In addition, PVDF is also an electronic and ionic insulator, which increases the internal resistance. Water-soluble binders with the advantages of low cost, safety, and environmental friendliness are more attractive and have been utilized in organic electrolyte Li-ion battery electrodes.^{6–8} Recently, the water-soluble binders (Ca-alginate, guar gum, xanthan gum, carboxymethyl chitosan, carboxymethyl cellulose, cyclodextrin, and polyacrylic acid) have displayed better performance than PVDF for alloy anodes and lithium metal oxide cathodes.9

Among water-soluble polymers, sodium alginate (SA) is a natural polysaccharide composed of β -D-mannuronic acid and α -L-guluronic acid, which contains a large number of carboxyl moieties to provide a strong adhesion to active materials in the electrodes. The SA binder in the silicon anode provides a strong interaction between SA and silicon particles enabling a much better cycle and rate performance of the Si anode than that using the PVDF binder.^{18,19} However, because SA is soluble in water, it can only be applied in organic electrolyte batteries.

SA has a large number of free carboxyl and hydroxyl groups along the SA backbone, which endow SA with the excellent feature to cross-link with divalent or trivalent metal ions to form a water-stable solid material. SA can be cross-linked in divalent or trivalent metal ion electrolytes and function as a binder in aqueous divalent metal ion batteries. In this work, we used aqueous Zn-ion batteries to demonstrate the effective enhancement of the cross-linked SA binder on performance. As one of the most promising energy storage devices, aqueous divalent metal ion-Zn²⁺-ion batteries (ZIBs) have received much attention owing to the high abundance in nature and a high theoretical specific capacity of 820 mAh g⁻¹ of Zn.^{20,21} However, aqueous Zn batteries still suffer from two critical challenges: low Zn plating/stripping Coulombic efficiency due to water decomposition²²⁻²⁴ and poor cycle stability of cathodes due to the dissolution in aqueous electrolytes and a

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Figure 1. Chemical structures of SA (a) and PVDF (b); photos of SA in aqueous solution (c) and PVDF in NMP solution (d); (e) after adding the electrolyte to panel (c); (f) after adding the electrolyte to panel (d); (g) FT-IR spectra of pristine PVDF and SA after adding different metal salt solutions.

large volume change during Zn insertion/extraction.^{25–27} To avoid the dissolution of the cathode materials and suppress water decomposition, we used a high concentration electrolyte (10 *m* ZnCl₂ to 4 *m* LiCl) and selected LiFePO₄ as a cathode that is very stable in the aqueous electrolyte. In the aqueous Zn-ion electrolyte, SA could cross-link with Zn²⁺ ions to form a strong bond for LiFePO₄ particles and enhance the mechanical strength of the cathode. The electrochemical performances of aqueous ZnllLiFePO₄ cells with cross-linked SA and traditional PVDF binders were symmetrically compared and characterized. Compared with the PVDF binder, the battery with the SA binder exhibited high specific capacitance, long cycle life, and better safety.

2. EXPERIMENTAL SECTION

2.1. Material Synthesis. The LiFePO₄ (LFP, Sigma-Aldrich) cathode was prepared by a conventional coating method. SA (Sigma-Aldrich) was dissolved in deionized water with a concentration of 5 wt %, while PVDF (Sigma-Aldrich) was dissolved in NMP (>99%, Sigma-Aldrich) solvent with a concentration of 10 wt % at room temperature. The LFP powder was mixed with carbon black (CB, Ketjen Black International Co., Japan) and the SA binder in a weight ratio of 8:1:1, grinding for 1 h to form a uniform slurry. As a comparison, the slurry with PVDF was prepared in the same way. To investigate the electrochemical property of SA and PVDF, the slurry that only contained binders and CB was prepared. The slurry was coated onto a 10 μ m-thick Ti foil (99.99% purity) and dried at 100 °C for 12 h to remove the solvent thoroughly. The electrodes that were labeled as LiFePO4/C/SA and LiFePO4/C/PVDF representing the electrodes prepared with the SA binder and PVDF binder, respectively.

2.2. Material Characterization. Fourier transform infrared (FT-IR) spectroscopy (Vector-22 spectrometer, Bruker, Germany) was used to analyze the structure of two binders. X-ray diffraction (XRD) was performed on an X-ray diffractometer (Rigaku SmartLab, Japan) equipped with a Cu target X-ray tube (40 kV; 150 mA; step size, 0.01°; scan rate, 10° min⁻¹; 10° < 2θ < 80°). The morphologies of the LFP electrodes were observed by a JSM-7610F field emission scanning electron microscope equipped with an energy-dispersive spectroscopy detector (EDS). Thermal gravimetric analysis (TGA)/ differential scanning calorimetry (DSC) measurements were conducted on a STA6000 synchronous thermal analyzer (PerkinElmer) in a nitrogen atmosphere with a heating rate of 10 °C min⁻¹ from 25 to 750 °C. The dynamic contact angle between anode pieces and the electrolyte was measured by a contact angle goniometer (HARKE-SPCA).

2.3. Electrochemical Measurement. The CR2032-type coin cells were assembled in a laboratory environment using LFP

electrodes as the cathode, Zn foil (99.99% purity) as the counter electrode, and a glass fiber diaphragm as the separator. The electrolyte consisted of 10 mol dm⁻³ ZnCl₂ (Sigma-Aldrich) and 4 mol dm⁻⁴ LiCl (Sigma-Aldrich). LFP electrodes were punched out with an area of 1 cm⁻², and the loading level was 2.0-2.2 mg cm⁻². To evaluate the cycle stability and rate performance, the cells were charged and discharged between 0.9 and 1.5 V galvanostatically on a Land-CT2001A battery tester (Wuhan, China). The calculated capacities were based on the weight of the LFP mass of the corresponding electrodes. Cyclic voltammetry (CV) testing and electrochemical impedance spectroscopy (EIS) measurements were conducted by a CH1660E impedance analyzer. CV was conducted at a scan rate of 0.5 mV s⁻¹ from 0.85 to 1.55 V (vs Zn/Zn^+). The temperature tolerance tests were performed in an incubator. EIS was measured by applying an alternating voltage of 5 mV over the frequency range from 10^{-2} to 10^5 Hz.

3. RESULTS AND DISCUSSION

3.1. Characterization of Cross-Linked SA. As shown in Figure 1a, SA and PVDF were dissolved in water and NMP, respectively. When the $ZnCl_2/LiCl$ aqueous electrolyte was added, SA cross-linked with Zn^{2+} ions to form a gel by coordination bonds. In contrast, no cross-link was observed in the PVDF/NMP solution after the aqueous electrolyte was added. Therefore, the high concentration of Zn^{2+} ions in the electrolyte and the SA in the electrode could cross-link to form a compact and water-insoluble layer on the electrode surface, which might strengthen the electrode material.¹⁸

FT-IR spectroscopy can investigate the molecular structure and functional groups in binders. The FT-IR spectra of the two binders are shown in Figure 1b. The FT-IR spectrum of SA displayed peaks at 3443, 1622, 1411, and 1028 cm⁻¹, which corresponded to the O-H stretching vibration, C=O stretching vibration, C-OH stretching vibration, and C-O stretching vibration in glucose units, respectively.²⁸ In the spectrum of PVDF, two typical peaks at 1190 and 1072 cm⁻¹ were related to the C-F stretching vibration.²⁹ It is worth noting that SA has an abundance of carboxyl and hydroxyl, which could promote the contact between the electrode material, conductive agent, and current collector and facilitate electrical and ionic conducting.¹¹ SA was immersed in LiCl (4 M) and $ZnCl_2$ (10 M)/LiCl (4 M) solutions for 4 h to investigate the interaction between SA and Zn^{2+}/Li^+ ions. Compared with the pure SA, the peaks of SA-LiCl did not move significantly, but the asymmetric stretching vibration peak of the -COO- group in SA-ZnCl₂/LiCl shifted to a higher wavenumber (from 1022 to 1036 cm⁻¹), which



Figure 2. (a) XRD patterns of LiFePO₄, LiFePO₄/C, LiFePO₄/C/SA, and LiFePO₄/C/PVDF; the red pattern was the standard spectrum of LiFePO₄ (JCPDS no. 40-1499), and the black pattern was the standard spectrum of titanium (JCPDS no. 1-1198). (b) TGA/DSC graph of SA in a nitrogen atmosphere.

demonstrated the formation of coordinate bonds between the carboxylate groups and Zn^{2+} ions.

3.2. Characterization of LiFePO₄ with the Cross-Linked SA Binder. The XRD diffraction patterns of the two electrode sheets are shown in Figure 2a. Obviously, all samples were crystalline in their natural states. The diffraction peaks of all samples matched the standard orthorhombic LiFePO₄ (JCPDS no. 40-1499). LiFePO₄/C/SA and LiFePO₄/C/ PVDF showed a special diffraction peak at the position of 40.5°, which was one of the characteristic peaks of titanium metal (JCPDS no. 1-1198). It indicated that the electrode sheets composed of SA and PVDF binders did not change the crystal structure of LiFePO₄/C.

The TGA/DSC thermograms of SA are presented in Figure 2b. The peak corresponding to absorbed water appeared and evolved at 60 °C. The graph showed a 12% weight loss from 60 to 150 °C, corresponding to a flatter absorption peak on the DSC curve. Another 36% weight loss from 200 to 270 °C corresponded to the fracture of the SA skeleton. The absorption peaks at 350 and 550 °C represented the decomposition of SA and carbonization of carbides, respectively.³⁰ Therefore, the electrodes with SA were dried in vacuum at 100 °C to remove absorbed water and could remain stable during the charge/discharge process.

To further investigate the stability of electrodes prepared with SA and PVDF in the aqueous electrolyte, electrode immersion experiments were studied. As shown in Figure 3a, the LiFePO₄/C/PVDF electrode was stable in both deionized water and the ZnCl₂/LiCl aqueous electrolyte. As shown in Figure 3b, when the LiFePO $_4/C/SA$ electrode was immersed in deionized water for 6 h, the slurry was peeled off severely from the titanium foil. However, the LiFePO $_{4}/C/SA$ electrode was stable in the aqueous electrolyte. Then, transferring the cross-linked LiFePO4/C/SA to deionized water, it still remained stable for 96 h. As presented in Figure 3c, SA could dissolve in water, so the cathode slurry dissociated in water molecules easily. However, after being immersed in the ZnCl₂/LiCl aqueous electrolyte, the carboxyl and hydroxyl groups of SA could cross-link with Zn²⁺ ions to form strong coordination bonds and networks. The networks strengthened the SA molecular chains and promoted the contacts between the conductive agent and positive electrode material (reducing the interface resistance). Therefore, the slurry did not fall off when it was immersed in deionized water again. In addition, the hydrophilic nature of cross-linked SA also promoted the electrolyte penetration into porous LiFePO₄ electrodes. The



Figure 3. (a) LiFePO₄/C/PVDF electrode immersed in deionized water and the ZnCl₂/LiCl aqueous electrolyte for 6–72 h; (b) LiFePO₄/C/SA electrode immersed in deionized water for 6 h and the ZnCl₂/LiCl aqueous electrolyte for 72 h, subsequently transferred to deionized water for 96 h; (c) schematics of electrodes immersed in solution; (d) dynamic contact angle photos of the electrolyte on LiFePO₄/C/SA and LiFePO₄/C/PVDF electrode sheets.

contact angle measurement was applied to demonstrate the high wettability of the prepared electrodes. Figure 3d shows the contact angle of the electrolyte on LiFePO₄/C/SA and LiFePO₄/C/PVDF electrode sheets. The contact angle of the PVDF electrode changed little within 60 s (reduced from 108.0 to 106.4°) while reduced from 81.1 to 52.8° on the SA electrode. Obviously, the LiFePO₄/C/SA electrode had better wetting tendency, which could result from the fact that the carboxyl and hydroxyl groups contained in SA enabled the electrode to be wetted in the water electrolyte more easily.

3.3. Electrochemical Performances of ZnllLiFePO₄ **Cells.** The cyclic stability of the LiFePO₄/C fabricated by the SA and PVDF binder has been examined through charge/ discharge tests at a current rate of 0.2 C (Figure 4a). The LiFePO₄/C/SA showed an initial discharge capacity of about 149 mAh g⁻¹ and a perfect capacity retention of 93.7% after 100 charge/discharge cycles with a CE of ~100%, compared to a capacity retention of 84.7% of the LiFePO₄/C/PVDF



Figure 4. Electrochemical performance of the LiFePO₄ electrode with the SA and PVDF binder. (a) Cycle performance between 0.9 and 1.5 V at a 0.2 C rate; (b) specific capacities of the sample at different rates; (c) cycle performance between 0.9 and 1.5 V at a 2 C rate; (d) charge/discharge curves at 0.2 C for dynamic contact angle photos of the LiFePO₄/C/SA and LiFePO₄/C/PVDF electrode sheets in the electrolyte; (e) discharge curves at 0.5 C for the LiFePO₄/C/SA electrode between -5 and 55 °C; (f) third charge/discharge curves at 0.5 C for the LiFePO₄/C/SA electrode between -5 and 55 °C;

electrode. Figure 4b displays the rate performances of LiFePO₄/C/SA and LiFePO₄/C/PVDF electrodes. The test rates were increased gradually from 0.2 to 5 C and finally returned back to 0.2 C. At 1 C, the LiFePO4 electrode delivered discharge capacities of 134.8 and 128.1 mAh g^{-1} with SA and PVDF, respectively. When the rate increased to 5 C, the LiFePO₄/C/SA electrode showed a higher discharge capacity of 113.3 mAh g⁻¹, corresponding to a capacity retention of 75.8% at 0.2 C, compared with a discharge capacity of 103.9 mAh g⁻¹ at 5 C and a capacity retention of 69.6% at 0.2 C for LiFePO₄/C/PVDF. When the rate turned back to 0.2 C, the discharge capacity increased to 148.5 and 143.1 mAh g⁻¹ SA and PVDF binders, respectively. In addition, the whole batteries with LiFePO₄/C/SA and LiFePO₄/C/PVDF electrodes displayed a long-term cycle life with capacity retention ratios of 83.5 and 71.2% after 500 cycles at 2 C, respectively (Figure 4c).

The charge/discharge curves of electrodes (Figure 4d) with different binders in the 3rd and 100th cycles were utilized to explore the differences in cycle performance. Both electrodes displayed a typical plateau at about 1.18 V (vs Zn/Zn^{2+}), corresponding to the electrochemical lithiation process of LiFePO₄. Compared to LiFePO₄/C/PVDF, the LiFePO₄/C/ SA electrode showed a broader discharge plateau and a higher discharge capacity, revealing faster electrode reaction kinetics and weak polarization. The voltage gap of the electrode increased, and the discharge capacity decreased when the charge/discharge cycle increased, which illustrated the impedance among electrode materials increased. The capacity of the LiFePO₄/C/SA electrode decayed slowly, and the voltage gap was smaller than that of the LiFePO₄/C/PVDF electrode.

The electrochemical performances of $LiFePO_4/C/SA$ and $LiFePO_4/C/PVDF$ electrodes were also evaluated from 55



Figure 5. Nyquist plots of LiFePO4 electrodes with different binders (a) before cycling and (b) after 100 cycles at 0.2 C.

down to -5 °C at 0.5 C (Figure 4e,f and Figure S1). Apparently, the discharge capacity decreased with the decrease of temperature. At 55 °C, LiFePO₄/C/SA had the highest initial capacity of 150.0 mAh g⁻¹ with a capacity retention of 88.4% after 50 charge/discharge cycles. Although the initial discharge capacity reduced to 100.5 mAh g^{-1} of LiFePO₄/C/ SA when the temperature was lowered to -5 °C, a higher capacity retention of 97.3% was obtained after 50 charge/ discharge cycles. After the immersing process, the cathode electrode could soak the electrolyte and get wet, wherein the SA binder dissolved in the electrolyte in the cathode and reacted with Zn²⁺ ions. As the viscosity of the SA-ZnCl₂ solution may increase greatly as the temperature drops (Figure S2), the SA binder may endow the cathode electrode with better mechanical strength at -5 °C. Compared with the electrochemical performances of LiFePO₄/C/PVDF between 15 and 55 °C, the LiFePO₄/C/SA had higher initial discharge capacity and capacity retention. Particularly, when the temperature reduced to -5 °C, the capacity retention of the SA electrode (97.3%) was 5% higher than that of the PVDF electrode (92.3%), which indicated that the SA binder had better performance than PVDF at low temperature.

Electrochemical impedance spectroscopy (EIS) can reflect the interface impedance and ion diffusion between electrode materials. The EIS spectra of LiFePO₄/C/SA and LiFePO₄/C/ PVDF electrodes are compared in Figure 5. The spectra was composed of two parts: a depressed semicircle in the high to medium frequency region and a straight line in the low frequency range. A typical equivalent model (Figure 5, inset) and the impedance parameters for different electrodes (Table 1) were obtained, where Re is the ohmic resistance, CPE represents the constant phase element, Rct is the chargetransfer resistance, and the inclined lines displayed in low frequency for both electrodes represent the Warburg impedance (Wo).³¹ Before the charge/discharge cycle, Re values of both electrodes were low, but Rct of the LiFePO₄/C/

Table 1. Impedance Parameters of LFP Electrodes with Two Binders

	before cycle		after the 100th cycle			
binders	Re (Ω)	Rct (Ω)	Re (Ω)	Rct (Ω)	$\sigma_{ m w}~(m s^{-0.5})$	
PVDF	4.2	14.1	11.5	206.9	153.6	
SA	4.1	4.1	13.5	82.5	69.0	

SA electrode was lower than that of the LiFePO₄/C/PVDF electrode. The phenomenon might be ascribed to the good electronic and ionic transportation in the LiFePO₄/C/SA electrode containing various hydrophilic groups. After the 100th cycle at 0.2 C, the Re of both electrodes increased. The Rct of the LiFePO₄/C/SA electrode was much lower than that of the LiFePO₄/C/PVDF electrode, which might be due to the fact that PVDF had fewer hydrophilic functional groups.

The CV curves of LiFePO₄/C/SA and LiFePO₄/C/PVDF electrodes are displayed in Figure 6, which illustrated that both electrodes had perfect reversibility. In Figure 6a, the voltage differences between the redox peaks of LiFePO₄/C/PVDF in the first two circles were both 0.310 V. However, the difference reduced to 0.278 V of LiFePO₄/C/SA (Figure 6b), which represented lower electrode polarization. Therefore, results indicated that the LiFePO4/C/SA electrode had better rate and low temperature performance and lower Rct and electrode polarization than the LiFePO4/C/PVDF electrode, which could be illustrated by the fact that SA contained lots of carboxyl and hydroxyl functional groups that could cross-link with Zn²⁺ ions to from strong cross-linked networks. The networks could combine CB and the active material tightly and, in addition, accelerate the diffusion of ions during the charge/discharge process.

3.4. Surface Morphology of LiFePO₄ Cathodes. The surface morphologies of the electrodes prepared with SA and PVDF binders were observed to investigate their electrochemical properties. Figure 7a shows the elemental mapping images of the two electrode sheets. Fe, Na, and C were dispersed evenly, indicating the uniform distribution of the SA binder on the electrode sheet. Figure 7b shows the scanning electron microscopy (SEM) images of electrodes and the schematic of electrodes with SA and PVDF before the first cycle and after the 100th cycle. Both SA and PVDF binders coated the slurry uniformly and smoothly. After 100 charge/ discharge cycles at a 0.2 C rate, the LiFePO₄/C/PVDF electrode appeared to have many cracks, which could cause the peeling of the active material from the electrode sheet and lead to capacity degradation. However, after 100 cycles, the LiFePO₄/C/SA electrode maintains better integrity, which was attributed to the fact that the cross-linked network formed by SA and Zn²⁺ ions could fix the electrode material firmly (Figure 7c). Furthermore, the interaction in the electrode could further reduce the interface impedance between the

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Figure 6. CV curves of the (a) LiFePO₄/C/PVDF and (b) LiFePO₄/C/SA electrodes.



Figure 7. Surface morphologies of electrodes: (a) elemental mapping of LiFePO₄/C/PVDF and LiFePO₄/C/SA electrode sheets; (b) morphologies of electrodes; (c) schematic of the electrodes with SA and PVDF binders in the initial and final cycles.

electrode and the electrolyte, which endows the $\text{LiFePO}_4/\text{C}/\text{SA}$ electrode with better electrochemistry performance.

4. CONCLUSIONS

In summary, SA was utilized as a binder for the cathode in the ZnllLiFePO₄ battery with the aqueous electrolyte for the first time. The water-soluble SA binder cross-linked with Zn²⁺ ions contained in the electrolyte to form a mechanically strong water-insoluble binder. After cross-linking, the insoluble network structure formed by Zn-SA could strengthen the mechanical property of the electrode material to resist the damage during the charge/discharge process. Different from the commercial PVDF binder, the LiFePO₄/C/SA cathode showed better electrochemical kinetics, smaller interface resistance, and better electrochemistry performance, even at low temperature $(-5 \, ^{\circ}C)$. In addition, SA could effectively improve the electrode integrity and enhance interfacial layer stability. The LiFePO $_4/C/SA$ showed a higher initial discharge capacity of about 149 mAh g⁻¹ and a perfect capacity retention of 93.7% after 100 charge/discharge cycles with a CE of \sim 100%, compared to a capacity retention of 84.7% after cycles of the LiFePO₄/C/PVDF electrode. These results proved that SA could be adopted as an environmental friendly watersoluble binder for the electrode in the Zn-Li aqueous battery. More importantly, this study illustrated that the water-based SA binder can be applied not only in non-aqueous systems but also in an aqueous system battery under certain conditions.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c02995.

Electrochemical performance of the LiFePO₄/C/PVDF electrode and viscosities of SA and PVDF (PDF)

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Notes

The authors declare no competing financial interest.

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