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Imidazolium based and pyrrolidinium based poly(ionic liquid) binders for hard carbon anode in sodium ion secondary batteries

This study systematically evaluated the electrochemical performance of 3 poly(ionic liquid) binders—PEVIFSI, PDADMAFSI, and PDADMATFSI with PVDF as control in sodium-ion batteries (SIBs) with hard carbon anodes. Figure 1 shows the synthesis routine of these binders, among them, PEVITFSI has low glass transformation temperature and exhibits viscoelasticity at room temperature, therefore excluded as a candidate for binder.

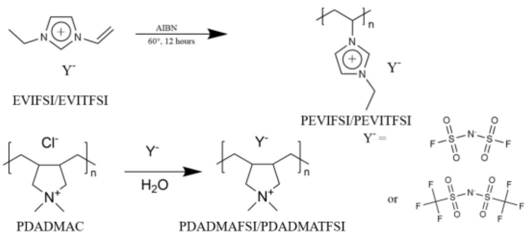
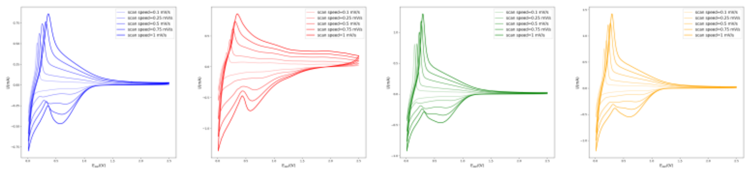


Figure 1 Synthesis routine of PEVIFSI, PEVITFSI, PDADMAFSI, PDADMATFSI binders

Figure 2 and Table 1 shows the result of Cyclic voltammetry (CV) test and overpotential. In CV test, PDADMAFSI and PDADMATFSI binders exhibited lower overpotentials (0.1402 V and 0.1367 V) and lower desodiation potentials compared to PVDF and PEVIFSI. Figure 3 shows the result of long cycle study, in half-cells using hard carbon anodes and assembled with PDADMATFSI as the binder, superior cycling stability and higher capacity retention (80.9%) were observed at a current density of 50 mA/g, compared to 77.8% for PVDF. PDADMAFSI also exhibited excellent cycling stability, though with a slightly lower capacity retention (67.7%).



PVDF PEVIFSI PDADMAFSI PDADMATFSI

Figure 2 Cyclic voltammetry (CV) test of hard carbon based half cell (sodium ion battery) fabricated by using different binders

Scan speed	PVDF	PEVIFSI	PDADMAFSI	PDADMATFSI
0.1	0.169	0.163	0.1488	0.1563
0.25	0.2056	0.2197	0.1855	0.1929
0.5	0.2556	0.2696	0.2322	0.2263
0.75	0.3023	0.3129	0.2624	0.2596
1	0.3559	0.3462	0.289	0.293
overpotential	0.1869	0.1832	0.1402	0.1367

Table 1 overpotential of all half cell fabricated by different binders

These binders also significantly reduced the solid electrolyte interphase (SEI) impedance, In Electrochemical Impedence Spectra(EIS) test and the simulation based on equivalent circuit, we found the SEI impedance shows values of 0.9147 Ω for PDADMAFSI, 0.4668 Ω for PDADMATFSI, and 4.564 Ω for PVDF. These results highlight the advantages of PDADMATFSI binder in sodium-ion batteries, showcasing their potential for improving electrochemical performance through enhanced stability and reduced resistance. Additionally, half-cells assembled with PEVIFSI as the binder exhibited significantly higher solid electrolyte interphase impedance after cycling, with a value of 13.07 Ω, compared to other binders.

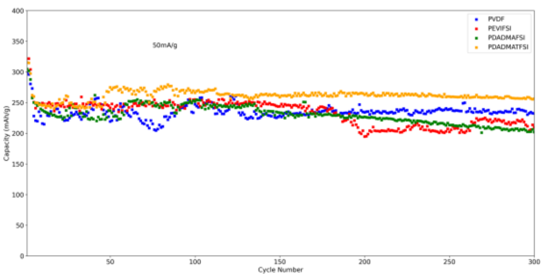


Figure 3 long cycle study of all half cell fabricated by using different binders

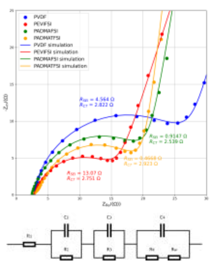
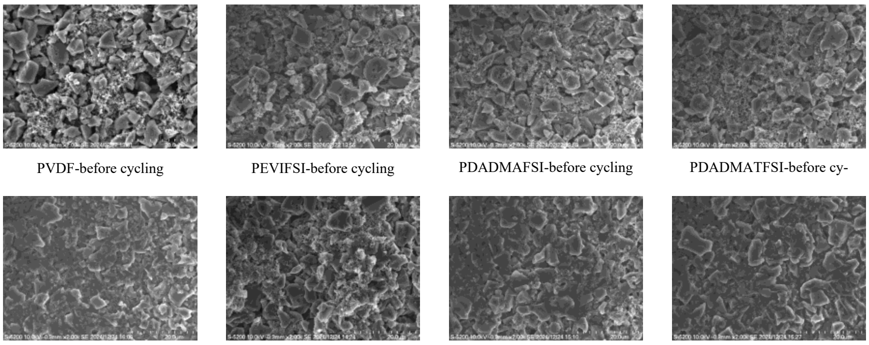


Figure 4 Electrochemical Impedence Spectra of hard carbon based half-cells with different binders after cycling and its equivalent simulation circuit

Morphological analysis via SEM further corroborated these findings. Figure 5 shows the image of the electrode surface before and after 300 cycle. The electrodes with PEVIFSI exhibited grooves and voids after cycling, confirming degradation, while the other binders maintained more uniform electrode surfaces.

In conclusion, PDADMA cation based binders, especially PDADMATFSI binder outperformed other binders in terms of electrochemical stability, cycling performance, and SEI properties, making it promising candidates for SIB applications. The poor performance of PEVIFSI highlights the limitations of imidazolium-based ionic liquid binders due to solubility issues and SEI instability.

Chapter 1 provides a comprehensive overview of sodium-ion batteries (SIBs) and their binder systems, highlighting their critical roles in determining the electrochemical performance of SIBs. Chapter 2 introduces the synthesis and characterization of newly developed pyrrolidinium-based binders-PDADMAFSI and PDADMATFSI. Chapter 3 presents a detailed analysis of imidazolium-based binders-PEVIFSI and pyrrolidinium-based binders-PDADMAFSI and PDADMATFSI, chapter 4 is the conclusion.


PVDF-before cycling　PEVIFSI-before cycling　PDADMAFSI-before cycling　PDADMATFSI-before cy-

PVDF-after cycling　PEVIFSI-after cycling　PDADMAFSI-after cycling　PDADMATFSI-after cycling

Figure 5 SEM image before and after cycling of the hard carbon half-cell fabricated by using PVDF, PEVIFSI, PDADMAFSI, PDADMAT-FSI as binder respectively.

Keywords: Sodium ion battery, hard carbon anode, poly(ionic liquids), binder, ion exchange