

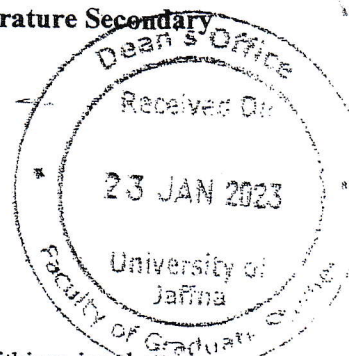
Synthesis and Characterization of Novel Gel-Polymer Electrolytes for Room Temperature Secondary Sodium-Ion Batteries

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ABSTRACT

Sodium-ion batteries are being widely investigated as cheaper alternatives to expensive lithium-ion batteries. However, synthesizing suitable electrolytes with sufficient ambient temperature ionic conductivities is one of the major challenges. This is mainly due to the larger size of Na^+ ions compared to that of Li^+ ions. Gel-polymer electrolytes (GPEs) are generally proposed as suitable candidates to enhance Na^+ ion mobility leading to sufficient ambient temperature ionic conductivities. In this work, five different sets of GPEs based on polymer hosts such as poly (ethylene oxide) (PEO), poly (methyl methacrylate) (PMMA) and poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) have been synthesized and characterized by Electrochemical Impedance Spectroscopy (EIS), DC polarization, Cyclic Voltammetry (CV), Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, X-ray diffraction (XRD) and Thermo-Gravimetric Analysis (TGA). Among PEO based electrolytes, the optimized composition, 7PEO-13 NaClO_4 -40EC-40PC (wt.%) showed an ambient temperature ionic conductivity of $9.5 \times 10^{-3} \text{ S cm}^{-1}$ and the variation of ionic conductivity with inverse temperature showed Arrhenius behavior with almost same activation energies for all the compositions. DC polarization studies on optimized composition revealed that the electrolyte is dominantly an ionic conductor ($t_i = 0.99$) with negligible electronic conductivity ($t_e = 0.01$), which is highly desirable for an effective electrolyte. As per CV studies, the optimized composition didn't show any redox peaks for a voltage window of -1.85 to +1.85 V. Absence of any crystalline peaks in the X-ray diffractograms of the GPEs is a clear evidence for the amorphous nature of these GPEs. Broadening of the FTIR vibrational bands at 1000-1300 and 1700-1850 cm^{-1} is ascribed to the lowering of crystallinity resulting from the formation of PEO/ Na^+ complex through Na^+ ion solvation within the polymer host. Another set of GPEs have been synthesized by using PMMA host polymer with different sodium salts; NaBF_4 , NaPF_6 , NaCF_3SO_3 and NaClO_4 . Among these, the composition 18PMMA-6 NaClO_4 -38EC-38PC (wt.%) showed the highest ambient temperature ionic conductivity of $3.7 \times 10^{-3} \text{ S cm}^{-1}$, and the conductivity variation with inverse temperature showed Arrhenius behavior with almost the same activation energies for all the compositions. DC polarization studies showed that the optimized composition is dominantly ionic conductor ($t_i = 0.99$) with negligible electronic conductivity ($t_e = 0.01$). The FTIR vibrational bands (950-1250 and 1680-1850 cm^{-1}) confirm the miscibility of polymer-salt complex. The optimized PMMA based composition mentioned above has been studied again with variety of plasticizer/solvent mixtures; EC/PC, EC/DMC and EC/DEC. Among these, PMMA- NaClO_4 -EC-DMC showed the highest ambient temperature ionic conductivity of $5.0 \times 10^{-3} \text{ S cm}^{-1}$, and the conductivity variation with inverse temperature followed Arrhenius behavior with almost the same activation energies for all the samples. As earlier, DC polarization studies on optimized composition confirmed that the electrolyte is dominantly an ionic conductor. Another set of PMMA based GPEs were also synthesized with EC/PC plasticizer/solvent mixture and the samples were investigated by EIS and Raman Spectroscopic techniques. The highest ambient temperature ionic conductivity of $4.2 \times 10^{-3} \text{ S cm}^{-1}$ was observed for 9PMMA-9 NaPF_6 -41EC-41PC (wt.%). Again, the variation of ionic conductivity with inverse temperature showed Arrhenius behavior with almost same activation energies for all the samples. In the Raman spectra, very sharp crystalline peaks of NaPF_6 in the range 400-850 cm^{-1} disappeared in the gel state of the electrolytes confirming the non-crystalline nature of these GPEs. Boson modes remain almost constant in intensity for all the six different compositions studied. Finally, a set of GPEs have been synthesized with PVdF-HFP host polymer and NaBF_4 salt. The GPE composition 6PVdF-HFP-14 NaBF_4 -40EC-40PC (wt.%) showed the highest ambient temperature ionic conductivity of $4.1 \times 10^{-3} \text{ S cm}^{-1}$. Variation of ionic conductivity with inverse temperature showed Arrhenius behavior with almost same activation energies. As in other sets of GPEs, DC polarization studies revealed that the optimized composition is dominant ionic conductor ($t_i = 0.99$) with negligible electronic conductivity ($t_e = 0.01$). TGA studies showed that these electrolytes are thermally stable almost up to 100 $^\circ\text{C}$ showing virtually no weight loss below this temperature. Overall, all five different sets of electrolytes studied in this work showed ambient temperature ionic conductivities in the order of $10^{-3} \text{ S cm}^{-1}$, which is sufficient for practical applications in sodium-ion batteries. Hence, synthesis routes developed and the data gathered in this study from various standardized techniques will be an important addition in the R&D works of sodium-ion batteries.

Keywords: Gel-polymer electrolytes, Sodium-ion batteries, Electrochemical impedance spectroscopy, Ionic conductivity, Arrhenius behavior



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