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Title :

Preparation and Characterization of PVC Based Polymer Electrolytes for Proton Batteries

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Searching a new material for the development of proton conducting polymer electrolytes that can be used in protonic electrochemical cells is the focus of this research study. In this study, the proton conducting polymer electrolytes were prepared by solution cast technique. Poly (vinyl chloride) PVC is used as the polymer host, ammonium triflate ($\text{NH}_4\text{CF}_3\text{SO}_3$) as the doping salt and ethylene carbonate (EC) and butyltrimethyl ammonium bis trifluoromethyl sulfonyl imide ($\text{Bu}_3\text{MeNTf}_2\text{N}$) is used as the plasticizers. Characterization techniques of EIS, XRD, FTIR, FESEM, DSC, TGA, transference number and linear sweep voltammetry measurements were used to study the properties of the PVC based proton conducting polymer electrolytes. Pure PVC exhibits room temperature ionic conductivity of $1.55 \times 10^{-10} \text{ S cm}^{-1}$. Various combinations of PVC and $\text{NH}_4\text{CF}_3\text{SO}_3$ compositions were attempted and the highest conductivity achieved was $2.50 \times 10^{-7} \text{ S cm}^{-1}$ when 30 wt. % $\text{NH}_4\text{CF}_3\text{SO}_3$ (A4) was incorporated into PVC which is an increase of about three orders of magnitude. The increase in conductivity with addition of $\text{NH}_4\text{CF}_3\text{SO}_3$ is attributed to increase in number of mobile ions and decrease in crystallinity of the films as shown by XRD, FESEM and DSC results. A further increase in ionic conductivity is observed when the polymer-salt electrolyte with the highest conductivity (A4) was added with plasticizers EC and $\text{Bu}_3\text{MeNTf}_2\text{N}$. The highest ionic conductivity achieved was $3.06 \times 10^{-5} \text{ S cm}^{-1}$ when 5 wt. % of EC (B1) was incorporated to the A4 polymer electrolyte. When 15 wt. % $\text{Bu}_3\text{MeNTf}_2\text{N}$ (C3) was added to the A4 polymer electrolyte, the highest ionic conductivity achieved was $1.56 \times 10^{-4} \text{ S cm}^{-1}$. Temperature dependence of conductivity study showed that conductivity increased with temperature and is found to obey the Arrhenius relationship. XRD studies showed that amorphous PVC becomes largely amorphous in nature upon addition of $\text{NH}_4\text{CF}_3\text{SO}_3$. Largely amorphous in nature is also obtained upon addition of EC and $\text{Bu}_3\text{MeNTf}_2\text{N}$ to PVC- $\text{NH}_4\text{CF}_3\text{SO}_3$. The degree of crystallinity, X_c is obtained by DSC and showed that the plasticized system has lower fraction of crystallinity compared to the salted systems with $\text{Bu}_3\text{MeNTf}_2\text{N}$ plasticized system having concentration of 15 wt. % (C3) having the least crystallinity. The transference number of this electrolyte is found to be 0.82 while its electrochemical window stability is 1.8 V. Electrochemical cells were fabricated using C3 electrolytes. The cells were discharged at different loads of 1.5 k Ω , 62 k Ω and 95 k Ω . The OCV of a cell based on the highest conducting electrolyte with configuration: $\text{Zn}+\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}+\text{PTFE} \mid 85 \text{ wt. \% (PVC-NH}_4\text{CF}_3\text{SO}_3) +15 \text{ wt. \% Bu}_3\text{MeNTf}_2\text{N (C3)} \mid \text{MnO}_2+\text{PTFE}$ is $\sim 1.52 \text{ V}$ while its discharge capacity is 0.55 mA h. The discharge performance of the cells showed that the protonic polymer electrolyte film proposed in this work has potential for application in protonic electrochemical cells for proton battery.

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