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Investigation of structural and morphological studies of Na^+ ion based TiO_2 nanocomposite PVDF-HFP/PVC solid polymer electrolytes

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Abstract. Sodium- ion conducting solid polymer electrolytes are considered a safe and sustainable alternative to liquid electrolytes for next-generation rechargeable batteries. In this work, nanocomposite membranes based on Poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and poly (vinyl chloride) (PVC) blend complexed with sodium tetrafluoroborate ($NaBF_4$) and reinforced with TiO_2 nanoparticles were fabricated by solution casting method. The recorded X-ray diffraction (XRD) patterns of these films revealed a significant reduction in polymer crystallinity upon the incorporation of salt and nanofiller, indicating enhanced amorphous character, which is favourable for ion transport. Scanning electron microscopy (SEM) confirmed a uniform dispersion of TiO_2 and the formation of a porous, interconnected microstructure at intermediate TiO_2 loadings. At higher filler concentrations, agglomeration and reduced porosity were observed, correlating with diminished structural uniformity. In brief, the findings confirm that TiO_2 nanofillers are capable of directing the morphology and chain packing of PVDF-HFP/PVC/$NaBF_4$ electrolytes, thereby paving the way for their use as solid electrolytes in sodium-ion energy storage systems.

1 Introduction

Designing solid-state electrolytes that have high ionic conductivity is one of the main issues in polymer research that needs to be addressed for electrochemical devices. Solid polymer electrolytes (SPEs) represent a very attractive material because they show good ionic conductivity, a wide electrochemical stability window, are light in weight, can be processed without solvents, and are mechanically flexible. Besides this, their non-leaking and safe character makes them especially compatible to be embedded in solid-state rechargeable batteries, in which energy density and safety during operation are of great importance [1-3].

Out of all the polymer hosts studied, PVDF-HFP and poly (vinyl chloride) (PVC) have been the most discussed in research papers. In particular, PVDF-HFP is liked for its high mechanical strength. It has semi-crystalline properties, and also, it can withstand high temperatures. The crystalline parts, which are for the most part coming from the segments of the vinylidene fluoride (VDF), give the material the necessary structural strength. While the

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addition of hexafluoropropylene (HFP is breaking the crystallinity, increasing the amorphous regions, and improving the flexibility of the chains. The combination of those two creates much better pathways for the movement of ions and thus the overall performance of the electrolyte is greatly enhanced [4,5]. On the other hand, poly (vinyl chloride) (PVC) is a thermoplastic material that is known for its good chemical stability, long-term durability, and ability to mix with different polymer matrices. When mixed with PVDF-HFP, PVC aids in the suppression of excessive crystallinity, increases the amorphous phase, and generates the condition that favors the dissociation of salt. The change together improves ionic conduction in the electrolyte system [6-8].

By blending different polymers, It is possible to assimilate their combined advantages and at the same time keep the ease of processing and the adjustable material properties. Several combinations such as PVDF-HFP/PVC, PVDF-HFP/PEO, and PVDF-HFP/PMMA have been deeply investigated as potential polymer electrolyte systems [7-9]. The blend of PVDF-HFP/PVC is especially significant out of all the different blends because apart from providing stable structural integrity thus it also promotes ion transport efficiently. Anion is a small, weakly coordinating, and easily dissociating species in polar polymer matrices. The electrochemical characteristic of polymer-salt complexes is further upgraded by the addition of nanofillers, among them TiO_2 nanoparticles have attracted much attention due to their large surface area, thermal stability, semiconducting behavior, and excellent photocatalytic properties. The incorporation of TiO_2 nano fillers into polymer electrolytes distributes the regular packing of the polymer chain lowers crystallinity and creates more ion migration channels, thus also stabilizing the electrode-electrolyte interface.

The TiO_2-implanted PVDF-HFP/PVC/$NaBF_4$ nanocomposite polymer electrolytes were produced using the solution casting in the current work. The structural and morphological features investigated and corelated by XRD (X-ray diffraction) and SEM (scanning electron microscope). The findings highlight the potential of nanofiller for effective strategy to optimize solid polymer electrolyte for solid state battery applications.

2 Experimental

2.1 Materials

Poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, Mw≈ 400,000, 99.99% purity) and poly (vinyl chloride) (PVC, Mw≈ 99,000, 99.99% purity) were procured from Sigma-Aldrich. Sodium tetrafluoroborate ($NaBF_4$, 98% purity, Sigma-Aldrich) was used as the sodium salt. Titanium dioxide (TiO_2) nano particles were employed as inorganic fillers. Acetone and Tetrahydrofuran were procured from Merk Millipore (Germany) and used without further purification.

2.2 Experimental

The nanocomposite membranes were prepared by the solution casting method. A constant polymer-salt matrix of 1000 mg PVDF-HFP:400 mg PVC:400 mg $NaBF_4$ was maintained. Different amounts of TiO_2 nanoparticles (10,20,30,40 and 50 mg) were incorporated as shown in Table 1, and the corresponding samples were designated as 3C1,3C2,3C3,3C4, and 3C5, respectively PVDF-HFP and PVC were dissolved in THF under continuous magnetic stirring for 12h, followed by further stirring for 5h to ensure complete miscibility. $NaBF_4$ was separately dissolved in THF for 2h. TiO_2 nanoparticles were dispersed in the salt solution and stirred for 2h to ensure uniform distribution. To get a uniform nanocomposite solution, the TiO_2-$NaBF_4$ solution was slowly added to the PVDF-HFP/PVC solution while stirring continuously for 5 hours. To eliminate any remaining solvent, the finished solution was cast onto glass Petri plates and then dried in a vacuum oven set at 60 °C. The 100-150 µm thickness was observed in the end free-standing films. All the samples were stored under vacuum until further characterization.

Table 1. Compositions of TiO_2 nanoparticles, $NaBF_4$ salt with PVDF-HFP and PVC polymers.

Sample code	Polymer PVDF-HFP (mg)	Polymer PVC (mg)	Salt $NaBF_4$ (mg)	Nanoparticle TiO_2 (mg)
3C1	1000	400	400	10
3C2	1000	400	400	20
3C3	1000	400	400	30
3C4	1000	400	400	40
3C5	1000	400	400	50

The Bruker D8 Advance X-ray diffractometer was used for structural investigation, Cu Ka radiation (λ = 1.5406 Å) at 40 kV and 30 mA. Using a step size of 0.02° and a scan rate of 2° min^{-1}, scans were acquired in the 2θ range of 10–70° Morphological characterisation was done using a 10-15 kV field-emission SEM (ZEISS). Images were recorded at different magnifications, and all micrographs include scale bars. Film thickness: Measured using a digital millimetre (0.8 mm accuracy).

3 Results and discussion

3.1 Structural analysis by XRD

X-ray diffraction (XRD) is a powerful technique for probing phase transitions and structural modifications in solid polymer electrolytes [10,11]. Figure 1 displays the XRD patterns of nanocomposite polymer electrolyte films based on PVDF-HFP: PVC: $NaBF_4$ with varying concentrations (0.555, 1.11, 1.665, 2.22, and 2.775 wt%) of TiO_2 nanoparticles, labeled as 3C1 to 3C5.The XRD patterns are plotted as intensity versus Bragg angle (2θ). In Figure 1(a), a distinct peak at $2\theta \approx 17.04°$ is observed, indicating the presence of a semi-crystalline phase in the sample with 0.555 wt% TiO_2 (3C1). As the concentration of TiO_2 nanoparticles increases from 0.555 wt% to 2.22 wt%, a progressive reduction in the intensity of the diffraction peaks is observed, suggesting a gradual disruption of the crystalline domains and enhancement of the amorphous phase.

The sample corresponding to 2.22 wt% TiO_2 (Figure 1(d)) exhibits a nearly featureless pattern, confirming a dominant amorphous structure. The change from crystalline to amorphous phase is credited to various interactions between the polymers of PVDF-HFP, PVC, the ionic salt $NaBF_4$, and nano TiO_2 particles. Besides the interaction of the fluorine atom of PVDF-HFP and the chlorine atom of PVC with the Na^+ ion of $NaBF_4$, the oxygen of TiO_2 also interacts with the Na+ ions. The increase in amorphous nature is very good for ion transport since it allows more segmental mobility and higher ionic conductivity. It is also worth noting that at 2.775 wt% of TiO_2 (Figure 1(e)), the peak intensity is slightly increased suggesting that a partial return of the semi-crystalline structure is happening, probably due to the aggregation of nanoparticles or saturation effects at the higher filler concentration.

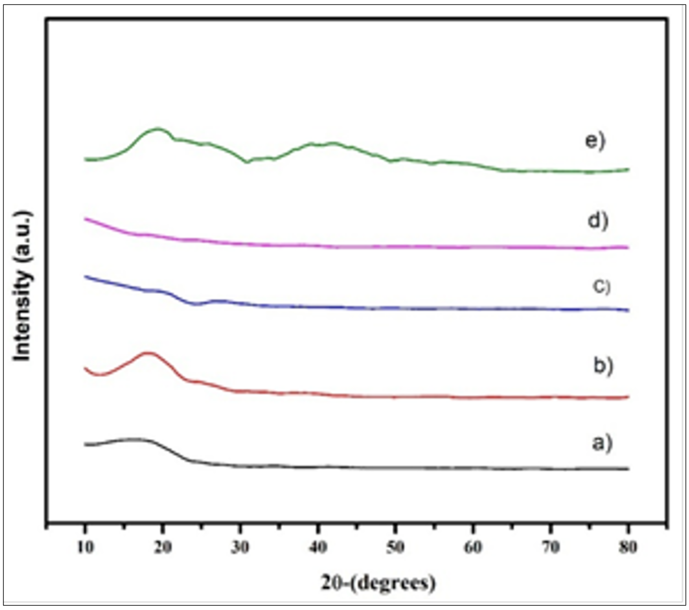

Fig. 1. XRD patterns of PVDF-HFP: PVC: $NaBF_4$ with TiO_2 of a) 3C1, b) 3C2 c)3C3, d) 3C4, and e) 3C5.

The XRD spectra reveal that the addition of TiO_2 nanofillers to PVDF-HFP: PVC: NaBF4 polymer electrolytes greatly changes the structural morphology. At 2.22 wt% TiO_2, an optimal amorphous phase can be seen, which confers the solid-state electrolytes with enhanced electrochemical performance.

3.2 Morphological studies by SEM

Figure 2 displays SEM micrographs of polymer electrolyte membranes made from PVDF-HFP, PVC, $NaBF_4$, and different concentrations of TiO_2 nanoparticles. The pictures help to understand the changes in the surface morphology, pore structure, and membrane microstructural properties caused by the nanoparticles. When TiO_2 nanoparticles are introduced into the PVDF-HFP: PVC: NaBF4 blend, we see noticeable changes in morphology across the samples. The initial compositions (Figure 2(a–c)) display uneven surface textures with isolated pore areas and a scattered distribution of particulate features. These inconsistencies indicate incomplete blending and limited porosity, which can hinder the effectiveness of ion conduction pathways.

An improvement in pore uniformity and distribution can be easily felt when TiO_2 concentration is raised. Figure 2d), relative to the sample with the best TiO_2 content, exhibits a mature porous structure with closely packed, evenly distributed micro-pores. Such a framework is supportive of the advanced amorphous phase that is perfect for the Na^+ ion transport via the membrane. The pore network of continuous and interconnected features is actually the result of the very strong interaction between PVDF-HFP, PVC, Na^+ ions, and Ti^{4+} from the TiO_2 nanoparticles. In these interactions, the suppression of crystallinity is accomplished and flexible ion-conducting channels formation is enhanced. The increase in porosity and a decrease in surface roughness of this sample is indicative of the success in the TiO_2 dispersion in the polymer matrix. The microstructure shown in Figure 2(d) is a clear indication of excellent amorphous nature and ionic mobility - the main features of high-performance polymer electrolytes for energy storage devices.

On the contrary, Figure 2(e) that illustrates the higher TiO_2 concentration, reveals a smoother surface along with an aggregation phase having reduced porosity. It implies a limit after which excess TiO_2 leads to the agglomeration, thus, fewer are the ion pathways and conductivity may be obstructed if the aggregation phase is a place where the Na^+ ions are trapped. The additional effort is being made to locate the precise mechanism and application to the electrochemical device.

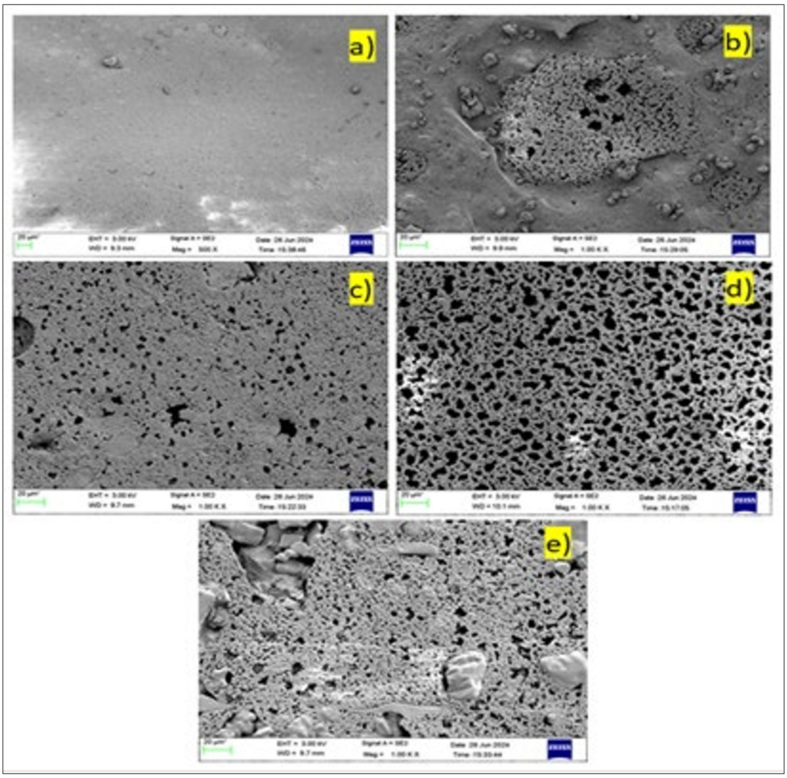

Fig. 2. SEM images of PVDF-HFP: PVC: $NaBF_4$ with TiO_2 of a) 3C1, b) 3C2, c)3C3, d) 3C4, and e) 3C5.

4 Conclusions

In this study, nanocomposite polymer electrolyte membranes comprising PVDF-HFP/PVC/$NaBF_4$ with TiO_2 nanofillers were successfully fabricated via the solution casting method. The main findings are XRD and SEM analysis confirmed that TiO_2 nanoparticles were uniformly dispersed within the polymer matrix at moderate filler loadings, producing a porous, interconnected microstructure favorable for Na^+ transport. At higher filler content, nanoparticle agglomeration reduced porosity and structural uniformity patterns revealed reestablishing semi-crystalline domains upon the addition of TiO_2. Further work is in-progress include electrochemical characterizations (ionic conductivity, transference number, electrochemical stability) to confirm practical applicability.

References

1. S. Ramesh, A. H. Yahaya, A. K. Arof. Dielectric behaviour of PVC-based polymer electrolytes, *Solid State Ionics,* **152,** 291-294, (2002). https://doi.org/10.1016/S0167-2738(02)00311-9
2. T.C Wen, H.S Tseng, T.T Cheng. Composite electrolytes comprising polytetramethylene/polypropylene glycol-based waterborne polyurethanes and polyethylene oxide via a mixture design approach.Ind.Eng.Chem.Res.**39**,72-78,(2000). https://doi.org/10.1021/ie990373c
3. B. Zhang, Y. Zhang, N. Zhang, L. Jun, L. Cong, J. Liu, S. Liqun, A. Mauger, M.J. Christian, X. Haiming, P. Xiumei. Synthesis and interface stability of polystyrene-poly (ethylene glycol)- polystyrene triblock copolymer as solid-state electrolyte for lithium-metal batteries.*J.Power Sources*.**428**,93-104, (2019). https://doi.org/10.1016/j.jpowsour.2019.04.033
4. M. Pourmadadi, A. Ahmari, M. Mirshafiei, Z. Omrani, F.Yazdian, A. Rahdar, M.A. Aboudzadeh. Polyvinylidene fluoride in biomedical applications: Properties, challenges, and future prospects. *European Polymer Journal*, 113889, (2025). https://doi.org/10.1016/j.eurpolymj.2025.113889
5. M. Usha Rani, Ravishanker Babu, S. Rajendran, Conductivity study on PVDF-HFP/PMMA electrolytes for lithium battery applications *Int. J. ChemTech Res.,* **5**, 1724, (2013).
6. R. Ying, Y. Zhoulan, D. Zhiying, G. Huajun, Y. Jing. A polymer electrolyte based on poly(vinylidene fluoride-hexafluoropylene)/hydroxypropyl methyl cellulose blending, *Electronic Materials Letters*, **14,** 342-347, (2018). https://doi.org/10.1007/s11581-012-0808-7
7. K. Amar, T. Sreekantha, A. Mallikarjuna, Maheshwar Reddy Mettu, M. Jaipal Reddy. Membrane formation of PVC and PVDF-HFP polymer blend, *Materials Today Proceedings,***92**, 561-564, (2023). https://doi.org/10.1016/j.matpr.2023.03.777
8. P. Ajay Kumar, Maheshwar Reddy Mettua, A. Mallikarjun, M. Jaipal Reddy, J. Siva Kumar. Morphological, structural, and thermal studies of polymer blend membranes of poly (vinylidene fluoride- hexaflouoropropylene) (PVdF-HFP) and poly (ethylene oxide) (PEO), *Materials Today Proceedings* **92**, (2023). https://doi.org/10.1016/j.matpr.2023.01
9. W. Shao, D. Nabb, N. Renevier, I. Sherrington, Y. Fu, J. Luo. Mechanical and Anti Corrosion Properties of TiO2 Nanoparticle Reinforced Ni Coating by Electrodeposition, *J. Electrochem. Soc*. **159** (11), D671–D676, (2012). https://doi.org/10.1149/2.065211jes
10. S. Ponmani and M.R. Prabhu. A study on the effect of bulky cations on the ionic conductivity and electrochemical performance of Mg-ion conducting poly(ionic liquids)s", *J.Mater.Sci.:Mater.Electron*.**29**,15086-15096, (2018). https://doi.org/10.1007/s10854-018-9649-0
11. L.M. McGrath, J. Jones, E. Carey, and J.F. Rohan. Ionic Liquid Based Polymer Gel Electrolytes for Use with Germanium Thin Film Anodes in Lithium Ion Batteries, *Chem.Open*.**8**, 1429, (2019). https://doi.org/10.1002/open.201900313