Physicochemical Characteristics of PVDF/ZSM-5 Composite Membrane for Potential Applications in Vanadium Redox Battery

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Article Info

Abstract

Composite membranes were synthesized using poly-(vinylidene fluoride) (PVDF) and zeolite (ZSM-5) to improve the performance of PVDF as a battery separator. The PVDF-ZSM-5 membranes, prepared with varying concentrations of ZSM-5, underwent characterizations of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). These analyses revealed a notable increase in β-phase formation in PVDF, greater porosity, and improved surface morphology due to the incorporation of ZSM-5. Evaluations of their physicochemical properties showed that these membranes resulted in electrical conductivity up to 96.4 mS/cm, enhanced contact area, porosity reaching 78.61%, and flux value up to 5.4×10^{-2} L m⁻² h⁻². Adjustments in ZSM-5 concentrations proved instrumental in fine-tuning these performance metrics. These findings highlight the potential of PVDF-ZSM-5 membranes as a cost-effective membrane separator for redox battery systems. This research lays the groundwork for future advancements and broader commercial applications in energy storage technology.

1. Introduction

According to the International Energy Agency (2024), global electricity demand is rising by an average of 3.4% annually, and it is expected to rapidly increase over the next three years. Economic growth, particularly in advanced and emerging economies, will further accelerate this demand. Consequently, adopting renewable energy sources is essential to meet rising global energy needs, along with the growing demand for high-performance batteries [1]. The rapid increase in global electricity demand has intensified the need for efficient and sustainable energy storage systems. Conventional power grids, often reliant on fossil fuel-based sources, are insufficient to address intermittency issues associated with renewable energy. As a result, advanced energy storage technologies have emerged as key enablers in the transition to cleaner energy solutions [2, 3]. Among these technologies, lithium-ion batteries (LIBs) have garnered significant attention due to their high energy density, fast response, and wide applicability in portable electronics and electric vehicles [4, 5, 6].

Over the past decade, substantial advancements in cathode materials, intercalation mechanisms, and battery architecture have contributed to the maturation of LIB technology [3, 7]. However, despite their advantages, LIBs face critical challenges such as safety risks, limited cycle life under heavy loads, and difficulties in large-scale applications due to thermal runaway and high material costs [8, 9]. To overcome these issues, researchers have explored alternative technologies, including redox flow batteries (RFBs), which offer enhanced flexibility, extended lifespan, and independent scaling of energy and power density [8, 9, 10]. In this context, the development of robust membrane separators is crucial for improving the efficiency and longevity of redox battery systems. Vanadium Redox Batteries (VRBs), for example, are promising large-scale energy storage systems due to their durability, flexible design, scalability, and environmentally friendly technology [11]. Ultimately, the potential of VRB technology is immense, offering a promising solution to the rising energy demands.

VRB consists of two electrolyte reservoirs and a stack of cells, in which an ion-exchange membrane separates each half-cell. The redox reactions occur at the respective electrodes during charging and discharging. It makes the greatest critical components in the VRB system, because a separator membrane prevents the intermixing of the positive and negative electrolytes. It not only separates the particular electrolytes, but also permits the transport of charge carriers to preserve the whole electroneutrality of the system [12, 13].

The most widely used cation-exchange membranes are Nafion series membranes, because of their high proton conductivity, flexibility, and good chemical stability in an oxidative environment. However, the system uses the perfluorosulfonic acid polymer membrane called Nafion, which is known for its high cost. As well as excessive vanadium ion crossover in the system, this is the limiting factor in the widespread commercialization of the VRB system [14, 15]. Given the high cost and limitations of the current Nafion series membranes, it is clear that alternative options for the membrane in the VRB system are needed. This necessity for innovation and change is what drives this research on PVDF-ZSM-5 membranes.

Some of the crucial aspects of the separator membrane that must be considered include the porosity of the membrane. Ion transport in the porous separator is based on the size-exclusion principle, wherein the mobility of the ions through the separator depends upon the Stokes radii of the hydronium ions (H_3O^+, 0.24 nm) and vanadium ions (more than 0.6 nm) [16]. Current research focuses on optimizing pore structures to facilitate H_3O^+ transport while blocking vanadium ions, thereby enhancing ion selectivity [17]. Based on these criteria, Poly(vinylidene fluoride) (PVDF) is one of the promising polymers for preparing battery separators.

PVDF is a non-reactive and pure thermoplastic fluoropolymer. It has been used as the Lithium battery separator [18]. PVDF is a bipolar polymer that arises from the strong electronegativity of fluorine atoms compared to carbon and hydrogen. It has high flexibility, higher chemical stability compared with other polymers, and great interfacial contact with electrolytes [19]. PVDF's organic solvent wettability is another merit, and ultimately, its relatively affordable price makes PVDF a proper selection for countless applications, such as battery separators [20]. PVDF is hydrophobic in structure, its native structure lacks ion-exchange sites, and tends to crystallize into the non-polar α-phase, reducing performance in electrochemical applications.

The significance of this research becomes clear when considering the need to enhance PVDF performance by reducing crystallinity, increasing hydrophilicity, and electronic uptake by inducing β-phase crystallization, thermal stability, and ion conductivity. A number of attempts were accomplished by incorporating various inorganic parts such as SiO_2 [21], Al_2O_3 [22], and TiO_2 [23]. Zeolite (ZSM-5), one of the candidate materials, a hydrated crystalline aluminosilicate composed of tetrahedral SiO_4^{4-} and AlO_4^{5-} units linked by oxygen atoms, forms a highly regular microporous structure [24, 25]. It was hypothesized that each AlO_4^{5-} unit would present a negative charge to the zeolite structure, which can be balanced by the structure's extra protons or metal cations [18]. Zeolite also possesses high adsorption and ion exchange properties and enhances the surface area. The incorporation of ZSM-5 zeolite addresses PVDF limitations by enhancing hydrophilicity, promoting β-phase crystallization, increasing porosity, and improving vanadium ion selectivity through its microporous, negatively charged framework.

This research focuses on the preparation of PVDF–ZSM-5 composites with varying amounts of PVDF and ZSM-5 to enhance the properties of PVDF. We investigated the physical and chemical characteristics of both components and evaluated their effects on hydrophobicity, electrical conductivity, porosity, and permeability. The hypothesis is that as the silica-to-alumina (Si/Al) ratio decreases, ZSM-5 becomes more hydrophilic and crystallizes in the β-phase, thereby improving its electrical conductivity and supporting the use of PVDF as a battery separator. The findings of this study are expected to contribute significantly to the development of VRBs, particularly in overcoming challenges related to high costs and excessive vanadium ion crossover.

2. Experimental

2.1. Synthesis of PVDF-ZSM-5 Membrane

The chemicals used in this study were polyvinylidene fluoride (PVDF, Sigma-Aldrich, >99.9%), ZSM-5 zeolite (Merck, Si/Al ratio = X, >99%, surface area ~425 m²/g), and dimethylacetamide (DMAc, Merck, 99.8%). All materials were used as received without further purification. PVDF–ZSM-5 membranes were synthesized using varying amounts of PVDF and ZSM-5 (Table 1).

PVDF (2.0 g to 1.4 g, depending on composition) was dissolved in 20 mL of DMAc, maintaining a fixed solvent-to-solid ratio of 10:1 (w/w). The mixture was stirred magnetically for 10 minutes at room temperature to ensure polymer dissolution. Furthermore, ZSM-5 (0-0.6 g) was poured into each beaker. The subsequent stirring was carried out for 12 hours at ambient conditions to promote homogeneous dispersion until a mixture was formed. The 12-hour stirring duration was selected based on standard practice and previous studies involving zeolite dispersion in polymeric matrices [26, 27]. The mixture was cast on a glass slide and left out for 15 minutes. The glass slide was then placed into a coagulation chamber containing water for 24 hours.

Table 1. PVDF and ZSM-5 weight variations in the synthesis of PVDF-ZSM-5 membrane

PVDF (g)	ZSM-5 (g)	Notation
2.0	0	A
1.8	0.2	B
1.6	0.4	C
1.4	0.6	D

2.2. Characterization of PVDF–ZSM–5 Membrane

The dried membrane was further characterized using Fourier Transform Infrared Spectroscopy (FTIR, Perkin-Elmer UATR Spectrum Two), operated in the range of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹; Scanning Electron Microscopy (SEM, JEOL JSM-6510LA SEM-EDX) at an acceleration voltage of 10 kV; and X-ray Diffraction (XRD, XRD-7000) using Cu Kα radiation (λ = 1.5406 Å), scanned over a 2θ range of 10°–80° at a scan rate of 2°/min. FTIR analysis was conducted to identify the functional groups present in the samples. SEM was used to examine the membrane morphology, while XRD was employed to assess the crystallinity of the materials.

2.3. Physicochemical Analysis of PVDF–ZSM–5 Membrane

The printed membrane was subjected to electrical conductivity, hydrophobicity, porosity, and permeability analysis. Electrical conductivity and drop shape analysis (DSA) were evaluated using the Ohaus conductivity meter, and the contact angle was observed using a high-resolution camera. The porosity test was conducted by immersing the membrane in demineralized water (aqua DM) for 24 hours at room temperature and then weighing the membrane. The membrane was dried in a vacuum oven at 60°C for 48 hours, and another weighing process was carried out. The magnitude of the membrane porosity was calculated using Equation (1).

$$\%Porosity = \frac{(W_{wet} - W_{dry})}{W_{wet}} \times 100\% \qquad (1)$$

Where, W_{wet} is the weight of the membrane after immersion in demineralized water, and W_{dry} is the weight of the membrane after complete drying.

The permeability was also tested by calculating the flux value after cutting the membrane to a 5 cm diameter and immersing the membrane in water for 48 hours at room temperature. The flux value was obtained by flowing 100 mL of water at 2 bar of air pressure. Furthermore, the volume of water that permeated through the membrane was collected and measured at 5-minute intervals until a steady value was obtained. The flux was then calculated using Equation (2).

$$J_w = \frac{\Delta V}{A \times t} \qquad (2)$$

Where, J_w is the flux (L m⁻² h⁻²), ΔV is the volume of permeate displaced (L), A is the effective membrane surface area (m²), and t is the time during which the permeate was stored (hours).

3. Results and Discussion

3.1. Characterization of PVDF–ZSM–5 Membrane

3.1.1. Characterization by XRD

The diffraction pattern of the PVDF-ZSM-5 membranes is shown in Figure 1. The diffraction patterns are strongly similar to the reference JCPDS 00-038-1638 for PVDF. The increasing concentration of ZSM-5 led to a change in the angle at the peak, and a diffraction peak was formed, but it did not change the phase of PVDF. PVDF has five forms of polymorphisms: α, β, γ, δ, and ε [28, 29].

When compared with the other polymorphisms, the beta phase has attractive properties for membrane applications due to its piezoelectric properties. The fluorine and hydrogen atoms in the β-phase are assembled in a zigzag shape, that considered to be the most stable form from a thermodynamic perspective [30].

The XRD pattern of pure PVDF (sample A) exhibited a dominant peak at 20°, corresponding to the characteristic reflection of the α-phase. No peaks were observed beyond this range, indicating the absence of the β-phase in the pure PVDF membrane. Upon the addition of ZSM-5, the XRD patterns of the PVDF–ZSM-5 composites showed no significant shifts compared to that of the pure PVDF membrane. The peak at 20°, associated with the α-phase, remained present but with reduced intensity, which further decreased with increasing ZSM-5 content [31].

Furthermore, increasing the ZSM-5 content to 0.6 g in sample D caused significant changes in the XRD pattern near 20°. A sharper, more intense peak at ~20.2° and a secondary peak at ~20.6° appeared, indicating the formation of the β-phase of PVDF. These changes suggest that ZSM-5 incorporation enhanced membrane crystallinity and promoted β-phase formation by providing additional nucleation sites and strong interfacial interactions between PVDF chains and the ZSM-5 framework. The sharper peaks indicate improved ordering within the crystalline domains of PVDF-ZSM-5 membranes at higher filler content. The highest peak of the shifting was obtained on sample D, indicating a strong interaction of PVDF and ZSM-5. Based on that, the stronger interaction between PVDF and ZSM-5 is expected to increase membrane strength.

3.1.2. Characterization by FTIR

FTIR analysis on the PVDF-ZSM-5 membrane was conducted to determine the functional groups in the membrane. As shown in Figure 2 and Table 2, all synthesized samples identified typical PVDF absorptions, such as C–H and C–C vibrations on 1400 cm⁻¹ and 1000 cm⁻¹, respectively. The formation of the ZSM-5 can be proven by a Si-O-Si vibration group at 800 cm⁻¹. The addition of ZSM-5 in sample D showed strong absorption of C–C vibration at 1000 cm⁻¹, indicating enhanced hydrophobicity of sample D due to covalent C–C bonding.
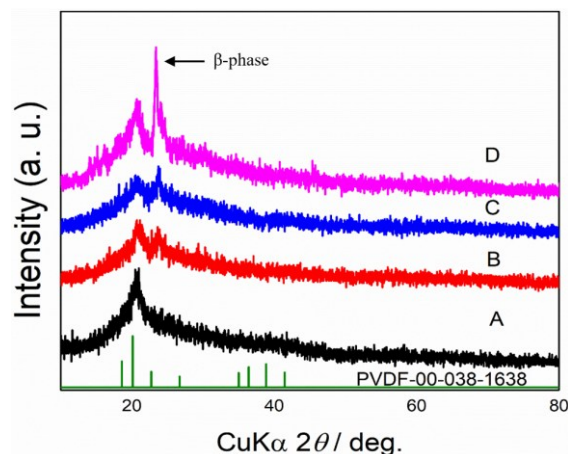

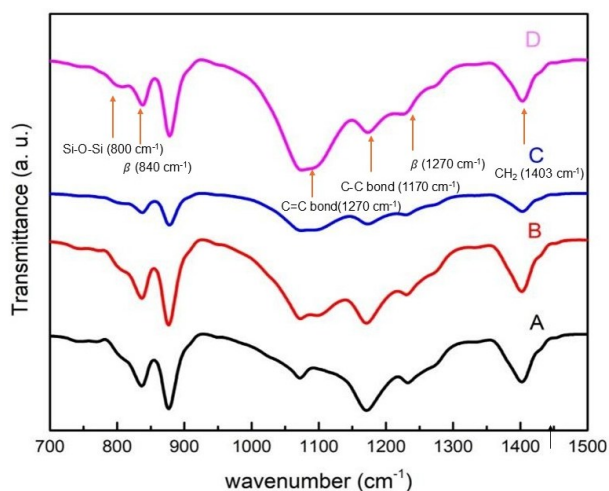**Figure 1**. XRD patterns of PVDF-ZSM-5 membrane (samples A-D)

Figure 2. FTIR spectra of the PVDF-ZSM-5 membrane (A–D)

Table 2. FTIR spectra analysis of PVDF-ZSM-5 membrane A-D [32]

Wavenumber (cm⁻¹)	Functional group
1400−1000	C−F stretching
1403	CH_2 vibration (PVDF)
1270	Asymmetric CF_2 stretching
1170	C−C vibration (PVDF)
1100−1200	C=C stretching
840	β-phase C−F stretching (PVDF)
800	Si−O−Si stretching (ZSM-5)
830−400	Si-O, Al-O, Na-O, K-O vibrations

Table 2 provides typical absorptions of PVDF and ZSM-5 functional groups. The functional group assignments apply to all membrane samples (A−D), which showed consistent characteristic absorption bands with minor intensity variations. Band assignments were matched to reports by Rahbari-Sisakht *et al.* [32]. Among the different polymorphisms of PVDF, only the β-phase has piezoelectric properties [33]. It can be identified in FTIR spectra by absorption bands near 840 cm⁻¹ (C−F stretching) and 1270 cm⁻¹ (CF_2 asymmetric stretching).

In the case of Sample D, a significant increase in the intensity of these characteristic peaks was observed, while the wavenumber positions remained constant. This indicates that the formation of the β-phase is driven by enhanced dipole alignment and molecular ordering, rather than changes in the vibrational energy states of the functional groups. The incorporation of ZSM-5 likely promotes the orientation of PVDF chains due to interfacial interactions, resulting in a higher degree of β-phase crystallinity without shifting the absorption bands.

3.1.3. Characterization by SEM

Asymmetrical particle structure patterns were formed through small granules and face surfaces. The synthesis through the phase inversion method will generally create the membrane with a more porous and asymmetrical microstructure. Due to its lower viscosity and solubility than pure PVDF, the increasing membrane porosity can alleviate particle agglomeration and form new granules. The addition of ZSM-5 to the PVDF has caused the membrane to become more porous. The formation of granules and porous microstructure proved the inhibition of solvent diffusion into the inner structure of the membrane [34].

The addition of ZSM-5 enhances pore development, leading to more interconnected voids and a rougher surface. Specifically, in sample D, the pore size ranges between approximately 150−300 nm, and regions with high pore density are clearly observed, indicated by a greater number of small-sized pores per unit area. Additionally, amorphous regions with less-defined boundaries and lower pore uniformity are present and annotated in the SEM image, presented in Figure 3. These features reflect the disrupted chain packing and increased surface heterogeneity caused by the dispersion of ZSM-5 particles, which enhance membrane permeability and ion transport efficiency.

3.2. Physicochemical Analysis of PVDF-ZSM-5 Membrane

3.2.1. Electrical Conductivity Analysis

Ionic conductivity is a key parameter that reflects the ability of a membrane separator to conduct ions. An ideal separator membrane should exhibit high ionic conductivity to ensure efficient ion transport. The electrical conductivity of the prepared PVDF−ZSM-5 membranes was measured using the two-point probe method, as presented in Table 3. The PVDF−ZSM-5 samples showed higher conductivity values compared to pure PVDF. This improvement is attributed to the porous nature of ZSM-5, which has a high intrinsic surface area that enhances electrolyte uptake when integrated into the polymer matrix.
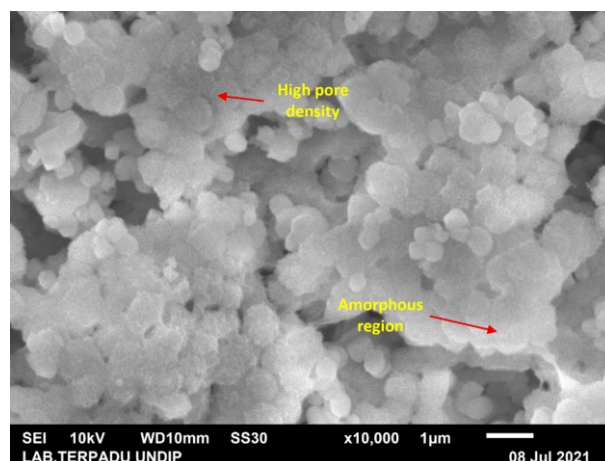

Figure 3. SEM image of the PVDF−ZSM-5 membrane morphology (SEI, 10 kV; WD: 10 mm; SS: 30; scale bar: 1 μm). Arrows indicate regions with high pore density (dark spots) and amorphous zones characterized by brighter areas with irregular structures
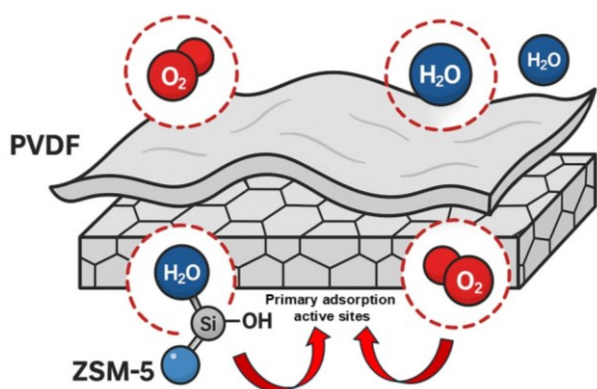
Figure 4. Schematic illustration of the PVDF/ZSM-5 composite model, potential adsorption sites for water and oxygen molecules

Moreover, the presence of zeolite particles helps suppress the growth of the surface resistive layer on the electrode by trapping impurities such as oxygen and water within their structure, thereby improving electrical conductivity [35]. This mechanism is illustrated in Figure 4. The negatively charged framework of ZSM-5 enables it to adsorb polar molecules like H_2O and O_2 through hydrogen bonding or van der Waals interactions within its porous network. By immobilizing these impurities, ZSM-5 prevents their interaction with the electrode interface, which in turn reduces resistive layer formation and enhances the ionic conductivity of the PVDF–ZSM-5 membrane.

The synergistic effect between the dielectric properties of PVDF and the adsorption capacity of ZSM-5 supports the membrane's potential application in electrochemical systems. However, samples with lower ZSM-5 concentrations exhibited insufficient stable ion transport channels. Among all samples, Sample D demonstrated the highest electrical conductivity, highlighting its potential to enhance battery performance [36].

3.2.2. Surface Contact Angle Analysis

Contact angle analysis was assessed using the DSA method, presented in Figure 5. The contact angle was calculated using ImageJ software. A small contact angle (<90°) indicates a high degree of wettability (hydrophilic) [37]. The contact angle is a principal parameter that affects the hydrophobicity of the battery separator [25]. As the water contact angle decreases, surface hydrophilicity increases. The contact angle values decreased in line with the ZSM-5 addition (Table 3). The

lowest contact angle value was observed in sample C, indicating greater wettability compared to neat PVDF. This improvement in wettability is attributed to the hydrophilic nature of the incorporated ZSM-5 particles. Although ZSM-5 generally increases hydrophilicity, the contact angle for sample D increases again to 125.69°, possibly due to altered surface morphology.

One of the key reasons ZSM-5 retains hydrophobicity is increased surface roughness and the high silicon-to-aluminum (Si/Al) ratio. Higher Si/Al ratio in ZSM-5 leads to a reduction in the number of Brønsted acid sites, which are typically associated with hydrophilicity. This reduction in acidic sites results in a more hydrophobic surface [38]. When the roughness enlarges, the hydrophobic separator of the surface contact angle rises as well. Furthermore, increased filler loading can lead to surface heterogeneity and aggregation that hinder water spreading [35, 39].

3.2.3. Porosity Analysis

Porosity analysis (swelling test) was conducted to evaluate the membrane's ability to absorb a constituent, which is a critical factor influencing ion transport in battery systems. Membrane porosity plays a key role in providing space for electrolyte retention, thereby facilitating ion movement. However, excessive or poorly controlled porosity can negatively affect battery performance. An imbalanced separator structure may result in pore fusion during operation, potentially causing rapid battery failure due to incomplete separator closure [19, 40]. Electrolyte uptake generally increases with rising porosity, particularly at higher ZSM-5 loadings. This enhancement in porosity supports improved ion transfer within the separator structure, contributing to better ionic conductivity [18, 20, 41].
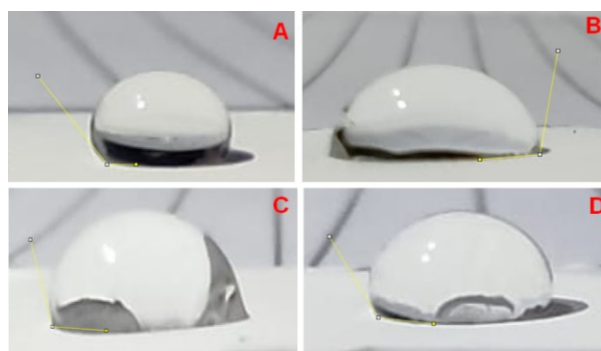

Figure 5. Droplet profiles for contact angles on the surface of the PVDF-ZSM-5 membrane

Table 3. Physicochemical analysis of PVDF-ZSM-5 membrane

Sample	Electrical conductivity (mS/cm)	Contact angle (°)	Porosity (%)	Flux value (L m^{-2} h^{-2})
A	61±1.2	126.927	83.29	2.2×10^{-2}
B	76.9±1.6	117.485	83.93	2.9×10^{-2}
C	81.8±1.5	104.506	77.36	3.5×10^{-2}
D	96.4±2.0	125.689	78.61	5.4×10^{-2}

The value of the membrane porosity was calculated using Equation 1. The porosity values ranged from 77.36% to 83.93%, exceeding the ideal threshold of 75% typically required for separator membranes (Table 3). The porosity percentage is influenced by the type and content of particles incorporated into the polymer matrix, particularly the addition of ZSM-5 [18, 36]. Although the overall porosity percentage decreased in samples C and D, this was accompanied by a significant increase in pore density—defined as the number of pores per unit area—especially in sample D. This distinction is crucial: sample A exhibited fewer but larger pores, resulting in higher total porosity, whereas sample D, with a higher ZSM-5 content, developed numerous smaller pores, forming a denser porous network. The ZSM-5 particles act as nucleating agents, disrupting the polymer matrix and creating multiple localized voids, thus increasing the number of small pores even though total pore volume may not be maximized.

3.2.4. Flux Value Analysis

Flux analysis was performed using water, with the highest flux value observed in sample D. In contrast, the sample without ZSM-5 exhibited the lowest flux. The variation in flux values with increasing ZSM-5 content can be attributed to structural changes within the membrane, including alterations in acid site density and hybridization with other components. These changes are associated with a reduction in both the rate constant and the sorption equilibrium constant.

The incorporation of zeolite into the PVDF−DMAc matrix enhances membrane permeability and selectivity. Zeolites possess a high surface area and intrinsic porosity, which contribute to increased water flux in membrane applications. Furthermore, studies have demonstrated that the addition of zeolite to PVDF membranes improves antifouling properties and enhances flux by modifying the membrane surface, rendering it more hydrophilic [42, 43].

The rate of this filtration can be influenced by several factors, such as membrane morphology and its intrinsic hydrophilicity [44]. The results indicate that each addition of ZSM-5 can affect the flux rate. According to Suryandari [37], the filtration process using a membrane is often hampered by small pore size, which can cause blockages, prolong separation time, and require higher operating pressures. The addition of ZSM-5 enhances membrane porosity, potentially improving filtration performance. Although porosity is commonly linked with increased permeability, flux is not always directly proportional to overall porosity percentage. As shown in Table 3, sample D exhibits a lower porosity (78.61%) compared to sample A (83.29%), yet delivers the highest flux value (5.4×10^{-2} L m^{-2} h^{-2}). This indicates that pore density—the number of small pores per surface area—plays a more critical role than porosity alone.

4. Conclusion

PVDF-ZSM-5 composite membranes with varying ZSM-5 concentrations, showcasing their physicochemical properties as potential separators for redox batteries. Integrating ZSM-5 into the PVDF matrix has led to a substantial enhancement in the membranes' physicochemical characteristics, such as electrical conductivity, porosity, and flux value. Structural assessments, including XRD and FTIR, revealed the development of the β-phase PVDF. Notably, the membrane with the highest ZSM-5 concentration exhibited the greatest electrical conductivity, demonstrating the positive impact of ZSM-5 incorporation. Interestingly, while ZSM-5 initially reduced hydrophobicity, enhancing wettability, higher concentrations adjusted the surface morphology and increased the contact angle, achieving a balance between hydrophilic and hydrophobic properties. The findings underscore the potential of PVDF-ZSM-5 membranes as an affordable membrane separator for redox battery systems.

Acknowledgement

References

[1] Rahul Sharma, Harish Kumar, Gaman Kumar, Saloni Sharma, Ranjan Aneja, Ashok K. Sharma, Ramesh Kumar, Parvin Kumar, Progress and challenges in electrochemical energy storage devices: Fabrication, electrode material, and economic aspects, *Chemical Engineering Journal*, 468, (2023), 143706 https://doi.org/10.1016/j.cej.2023.143706

[2] Theodore Azemtsop Manfo, Mustafa Ergin Şahin, Intercalation Reaction in Lithium-Ion Battery: Effect on Cell Characteristics, *The International Journal of Materials and Engineering Technology*, 6, 2, (2023), 70-78

[3] A. M. Theodore, Promising cathode materials for rechargeable lithium-ion batteries: a review, *International Journal of Sustainable Energy and Environmental Research*, 14, 1, (2023), 51-58

[4] Theodore Azemtsop Manfo, A Comprehensive Analysis of Material Revolution to Evolution in Lithium-ion Battery Technology, *Turkish Journal of Materials*, 8, 1, (2023), 1-13

[5] Theodore Azemtsop Manfo, Structural, electrical, and electrochemical studies of the olivine LiMPO$_4$ (M=Fe, Co, Cr, Mn, V) as cathode materials for lithium-ion rechargeable batteries based on the intercalation principle [version 1; peer review: 1 approved with reservations, 3 not approved], *Materials Open Research*, 2, 11, (2023), https://doi.org/10.12688/materialsopenres.17559.1

[6] Azemtsop Manfo Theodore, Progress into lithium-ion battery research, *Journal of Chemical Research*, 47, 3, (2023), https://doi.org/10.1177/17475198231183349

[7] Azemtsop Manfo Theodore, Abdullahi Abbas Adam, Pawan Singh Dhapola, Effect of Layered, Spinel, and Olivine-Based Positive Electrode Materials on Rechargeable Lithium-Ion Batteries: A Review, *Journal of Computational Mechanics*, 6, 4, (2023), https://doi.org/10.46253/jcmps.v6i4.a4

[8] Theodore Azemtsop Manfo, Mustafa Ergin Şahin, Development of an automatic photovoltaic cell-battery powered water irrigation system incorporated with Arduino software for agricultural activities, *Gazi Mühendislik Bilimleri Dergisi*, 10, 2, (2024), 314-328 http://doi.org/10.30855/gmbd.0705a07

[9] Theodore Azemtsop Manfo, Hannu Laaksonen, A review of carbon-based hybrid materials for supercapacitors, *New Carbon Materials*, 40, 1, (2025), 81-110 https://doi.org/10.1016/S1872-5805(25)60943-7

[10] Nacer Badi, Azemtsop Manfo Theodore, Saleh A. Alghamdi, Ayshah S. Alatawi, Adnan Almasoudi, Abderrahim Lakhouit, Aashis S. Roy, Alex Ignatiev, Thermal effect on curved photovoltaic panels: Model validation and application in the Tabuk region, *PLOS One*, 17, 11, (2022), e0275467 https://doi.org/10.1371/journal.pone.0275467

[11] Utsav Dalal, Anil Verma, Highly Economical and Efficient Polyethylene Separator for Vanadium Redox Flow Battery, *Energy & Fuels*, 38, 13, (2024), 12182-12191 https://doi.org/10.1021/acs.energyfuels.4c01685

[12] Zhen Jiang, Konstantin Klyukin, Kaellen Miller, Vitaly Alexandrov, Mechanistic Theoretical Investigation of Self-Discharge Reactions in a Vanadium Redox Flow Battery, *The Journal of Physical Chemistry B*, 123, 18, (2019), 3976-3983 https://doi.org/10.1021/acs.jpcb.8b10980

[13] Z. Yang, R. M. Darling, M. L. Perry, Electrolyte Compositions in a Vanadium Redox Flow Battery Measured with a Reference Cell, *Journal of The Electrochemical Society*, 166, 13, (2019), A3045 https://doi.org/10.1149/2.1161913jes

[14] Utsav Dalal, Manshu Kapoor, Anil Verma, Low-Cost Pore-Filled PVDF–Nafion Composite Membrane for the Vanadium Redox Flow Battery, *Energy & Fuels*, 37, 17, (2023), 13457-13466 https://doi.org/10.1021/acs.energyfuels.3c01932

[15] Ce Shi, Tingli Liu, Wenduo Chen, Fengchao Cui, Lunyang Liu, Yuyang Cai, Yunqi Li, Interaction, structure and tensile property of swollen Nafion® membranes, *Polymer*, 213, (2021), 123224 https://doi.org/10.1016/j.polymer.2020.123224

[16] Qi Zhang, Quan-Feng Dong, Ming-Sen Zheng, Zhao-Wu Tian, The preparation of a novel anion-exchange membrane and its application in all-vanadium redox batteries, *Journal of Membrane Science*, 421-422, (2012), 232-237 https://doi.org/10.1016/j.memsci.2012.07.024

[17] Utsav Dalal, Anil Verma, Low-cost and durable polyvinyl alcohol modified polyethylene separator for vanadium redox flow battery, *Journal of Energy Storage*, 100, (2024), 113413 https://doi.org/10.1016/j.est.2024.113413

[18] Majid Badini Pourazar, Toraj Mohammadi, Mohamad Reza Jafari Nasr, Omid Bakhtiari, Mehran Javanbakht, Preparation and characterization of poly(vinylidene fluoride)-13X zeolite mixed matrix membranes for lithium ion batteries' separator with enhanced performance, *Journal of Applied Polymer Science*, 137, 44, (2020), 49367 https://doi.org/10.1002/app.49367

[19] Carlos M. Costa, Maria M. Silva, S. Lanceros-Méndez, Battery separators based on vinylidene fluoride (VDF) polymers and copolymers for lithium ion battery applications, *RSC Advances*, 3, 29, (2013), 11404-11417 https://doi.org/10.1039/C3RA40732B

[20] Kyungho Hwang, Byeongmin Kwon, Hongsik Byun, Preparation of PVdF nanofiber membranes by electrospinning and their use as secondary battery separators, *Journal of Membrane Science*, 378, 1, (2011), 111-116 https://doi.org/10.1016/j.memsci.2011.06.005

[21] C. M. Costa, M. Kundu, V. F. Cardoso, A. V. Machado, M. M. Silva, S. Lanceros-Méndez, Silica/poly(vinylidene fluoride) porous composite membranes for lithium-ion battery separators, *Journal of Membrane Science*, 564, (2018), 842-851 https://doi.org/10.1016/j.memsci.2018.07.092

[22] Dezhi Wu, Lei Deng, Yu Sun, Kwok Siong Teh, Chuan Shi, Qiulin Tan, Jinbao Zhao, Daoheng Sun, Liwei Lin, A high-safety PVDF/Al$_2$O$_3$ composite separator for Li-ion batteries via tip-induced electrospinning and dip-coating, *RSC Advances*, 7, 39, (2017), 24410-24416 https://doi.org/10.1039/c7ra02681a

[23] Monali V. Bhute, Yogita P. Mahant, Subhash B. Kondawar, Titanium dioxide / poly(vinylidene fluoride) hybrid polymer composite nanofibers as potential separator for lithium ion battery, *Journal of Materials NanoScience*, 4, 1, (2017), 6-12

[24] João Nunes-Pereira, Manab Kundu, Attila Gören, Maria Manuela Silva, Carlos M. Costa, Lifeng Liu, Senentxu Lanceros-Méndez, Optimization of filler type within poly(vinylidene fluoride-co-trifluoroethylene) composite separator membranes for improved lithium-ion battery performance, *Composites Part B: Engineering*, 96, (2016), 94-102 https://doi.org/10.1016/j.compositesb.2016.04.041

[25] Jiawen Zhang, Yakang Xiang, Muhammad Imran Jamil, Jianguo Lu, Qinghua Zhang, Xiaoli Zhan, Fengqiu Chen, Polymers/zeolite nanocomposite membranes with enhanced thermal and electrochemical performances for lithium-ion batteries, *Journal of Membrane Science*, 564, (2018), 753-761 https://doi.org/10.1016/j.memsci.2018.07.056

[26] Roberto Navarro-Tovar, Patricia Gorgojo, Megan Jobson, Peter Martin, Maria Perez-Page, Innovations in water desalination: enhancing air gap membrane distillation performance by the incorporation of clay nanoparticles into PVDF matrix membranes, *Environmental Science: Water Research & Technology*, 10, 10, (2024), 2418-2431 https://doi.org/10.1039/D4EW00326H

[27] Dong Zou, Chang Hu, Enrico Drioli, Zhaoxiang Zhong, Engineering green and high-flux poly(vinylidene fluoride) membranes for membrane distillation via a facile co-casting process, *Journal of Membrane Science*, 655, (2022), 120577 https://doi.org/10.1016/j.memsci.2022.120577

[28] Jinqiang Cui, Jiuqing Liu, Chunfeng He, Jie Li, Xiufeng Wu, Composite of polyvinylidene fluoride–cellulose acetate with Al(OH)$_3$ as a separator for high-performance lithium ion battery, *Journal of Membrane Science*, 541, (2017), 661-667 https://doi.org/10.1016/j.memsci.2017.07.048

[29] Mi-mi Tao, Fu Liu, Bi-rong Ma, Li-xin Xue, Effect of solvent power on PVDF membrane polymorphism during phase inversion, *Desalination*, 316, (2013), 137-145 https://doi.org/10.1016/j.desal.2013.02.005

[30] Mohammed Alsultan, Effect of polymer dope solution temperature on the fabrication of flat-sheet polyvinylidene fluoride (PVDF) membranes: Water filtration and membrane distillation (MD) applications, Umeå University, 2021

[31] Yi Shen, Aik Chong Lua, Preparation and characterization of mixed matrix membranes based on PVDF and three inorganic fillers (fumed nonporous silica, zeolite 4A and mesoporous MCM-41) for gas separation, *Chemical Engineering Journal*, 192, (2012), 201-210 https://doi.org/10.1016/j.cej.2012.03.066

[32] Masoud Rahbari-Sisakht, Ahmad Fauzi Ismail, Takeshi Matsuura, Daryoush Emadzadeh, Long-term study of CO_2 absorption by PVDF/ZSM-5 hollow fiber mixed matrix membrane in gas–liquid contacting process, *Journal of Applied Polymer Science*, 134, 14, (2017), https://doi.org/10.1002/app.44606

[33] Zhanbin Qiu, Tingping Lei, Shuiping Li, Xiaomei Cai, Kai Yang, Insights into Polymorphic Transition of PVDF during Nonsolvent-Induced Phase Separation, *Macromolecules*, 57, 3, (2024), 1159-1168 https://doi.org/10.1021/acs.macromol.3c02394

[34] Haolong Bai, Xuan Wang, Yitong Zhou, Liping Zhang, Preparation and characterization of poly(vinylidene fluoride) composite membranes blended with nano-crystalline cellulose, *Progress in Natural Science: Materials International*, 22, 3, (2012), 250-257 https://doi.org/10.1016/j.pnsc.2012.04.011

[35] Majid Badini Pourazar, Toraj Mohammadi, Mohamad Reza Jafari Nasr, Mehran Javanbakht, Omid Bakhtiari, Preparation of 13X zeolite powder and membrane: investigation of synthesis parameters impacts using experimental design, *Materials Research Express*, 7, 3, (2020), 035004 https://doi.org/10.1088/2053-1591/ab7217

[36] Retno Ariadi Lusiana, Nor Basid Adiwibawa Prasetya, Khabibi Khabibi, Pengaruh Penambahan Aditif terhadap Karakterisasi Fisikokimia Membran Polisulfon, *Indonesian Journal of Chemical Science*, 9, 3, (2020), 194-200

[37] Ervin Tri Suryandari, Sintesis Membran Komposit PVDF-Zeolit untuk Penghilangan Metilen Biru, *al Kimiya: Jurnal Ilmu Kimia dan Terapan*, 6, 2, (2019), 58-66 https://doi.org/10.15575/ak.v6i2.6491

[38] Wenpeng Li, Gang Wang, Xinxin Wang, Wenqing Wu, Zeyu Zhao, Fenglian Zhang, Guoxia Jiang, Ganggang Li, Jie Cheng, Zhongshen Zhang, Zhengping Hao, Hydrophobic Porous Aromatic Framework as an Adsorbent for Effectively Selective Removal of Aromatic Volatile Organic Compounds, *ACS ES&T Engineering*, 4, 6, (2024), 1356-1366 https://doi.org/10.1021/acsestengg.3c00633

[39] Dong Hee Kang, Hyun Wook Kang, Surface energy characteristics of zeolite embedded PVDF nanofiber films with electrospinning process, *Applied Surface Science*, 387, (2016), 82-88 https://doi.org/10.1016/j.apsusc.2016.06.096

[40] Sheng Shui Zhang, A review on the separators of liquid electrolyte Li-ion batteries, *Journal of Power Sources*, 164, 1, (2007), 351-364 https://doi.org/10.1016/j.jpowsour.2006.10.065

[41] Z. Y. Zhang, T. B. Shi, C. Z. Jia, W. J. Ji, Y. Chen, M. Y. He, Adsorptive removal of aromatic organosulfur compounds over the modified Na-Y zeolites, *Applied Catalysis B: Environmental*, 82, 1, (2008), 1-10 https://doi.org/10.1016/j.apcatb.2008.01.006

[42] Beata Fryczkowska, Marta Sieradzka, Ewa Sarna, Ryszard Fryczkowski, Jarosław Janicki, Influence of a graphene oxide additive and the conditions of membrane formation on the morphology and separative properties of poly(vinylidene fluoride) membranes, *Journal of Applied Polymer Science*, 132, 46, (2015), https://doi.org/10.1002/app.42789

[43] Zuhriah Mumtazah, Reva Edra Nugraha, Arif Priyangga, Maktum Muharja, Rizki Fitria Darmayanti, Ditta Kharisma Yolanda Putri, Change of PVDF Ultrafiltration Membranes for Humus Acid Removal Applications in Water by Adding Fe_2O_3/Zeolite Additives, *The 3rd International Conference on Renewable Energy (I-CORE 2023)*, 2024 https://doi.org/10.1051/e3sconf/202447303007

[44] Alfian Yulia Rahmat, Intan Syahbanu, Rudiyansyah Rudiyansyah, Ultrafiltration Membrane of Polysulfone/TiO_2 (Psf/TiO_2) for Diesel Fuel Polluted Water Filtration, *Jurnal Kartika Kimia*, 3, 1, (2020), 7-12 https://doi.org/10.26874/jkk.v3i1.46