# Electrochemical behaviour of PBI-based vanadium redox flow battery membranes.

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**Abstract.** Energy Storage System (ESS) has a critical role in ensuring the reliability and efficiency of energy supply. The Vanadium Redox Flow Batteries (VRFBs) are a promising solution because it is reliable, fire-safe, and a sustainable energy storage system. However, the widespread adoption of VRFB is limited by high costs and inefficiencies that are found in Nafion-based membranes. This study presents the synthesis and electrochemical evaluation of phosphoric acid-doped Polybenzimidazole (PBI) membranes blended with Sulfonated Polyether Ether Ketone (SPEEK) at varying weight percentages (3 wt%, 5 wt%, and 10 wt%) named 3M A, 5M A and 10M A respectfully, for application in VRFBs. The objective was to enhance electrochemical stability preserving chemical and structural integrity in acidic vanadium electrolyte environments. Comprehensive characterization including polarization corrosion testing, was done to evaluate the corrosion resistance and electrochemical impedance spectroscopy (EIS) testing used to evaluate the proton conductivity of the membranes via Nyquist plots to contribute, to the overall electrochemical properties of the composite membranes. Notably, the 5 wt% SPEEK-PBI blend demonstrated superior electrochemical performance, exhibiting a low corrosion current density = ~0.48 µA/cm², a stable corrosion potential = 0.081 V, SPEEK showed best proton conductivity at 1.61 mS/cm. The findings position the 5M A membrane, followed by SPEEK as a promising alternative to Nafion, offering improved electrochemical stability in VRFBs and recommendation to carefully cater for membrane thickness after solution casting.

## 1 Introduction

In the current days, the demand for efficient ways of living and operating has never been greater, driven by the dual pressures of rising energy costs and the increasingly unreliable supply of electricity in many parts of the world, including South Africa. Frequent power disruptions, such as load-shedding or a phenomenon called load reduction, not only hinder economic productivity but also disrupt daily life, emphasizing the urgency for energy conscious living and the adoption of technologies that maximize energy efficiency. In this context, green energy solutions, such as renewable energy generation and advanced energy storage systems, are not just optional alternatives, but critical enablers of sustainable development. These alternatives offer significant means to reduce dependence on fossil fuels,

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lower carbon emissions, and ensure a stable, cost-effective, and environmentally clean energy supply. Embracing green energy is therefore central to achieving a more resilient, productive, and efficient lifestyle, aligning both individual, societal goals and with the broader global mandate for safer energy supply. The reliance on carbon-intensive energy systems, particularly fossil fuels such as coal, crude oil, natural gas, and heavy fuel oils, continues to intensify global carbon emissions while simultaneously depleting limited natural resources. These conventional energy sources dominate electricity generation and industrial processes in many countries, yet their extraction, processing, and combustion release substantial amounts of greenhouse gases, primarily carbon dioxide ($CO_2$) and methane ($CH_4$), which accelerate climate change and contribute to environmental degradation. To mitigate these challenges, the transition and inclusion of renewable energy technologies, emphasizing sustainability, operational efficiency, and grid stability has become imperative and highly important [1].The inclusion and transition of this critical and crucial renewable energy technologies needs to also focus on the development of advanced energy storage solutions (ESS) capable of addressing the intermittency of renewable sources (e.g., solar, wind) while ensuring reliable power delivery [3]. As the global transition to sustainable energy accelerates, the demand for fire-safe, scalable, affordable, and high-efficiency energy storage solutions has never been greater and of more importance [1]. The Vanadium Redox Flow Batteries (VRFBs) have emerged as a leading candidate for fire safe, long-duration energy storage due to their non-flammable electrolyte, deep discharge capability, and extended cycle life [2-4].

However, the widespread adoption and commercialization of VRFBs has been hindered by the high initial cost, driven not only by the expense of Nafion-based membranes, which remain the benchmark for ion-exchange performance but are costly to produce, other components are the price of vanadium electrolyte preparation, system balance-of-plant components (such as pumps, sensors, and control systems), and the capital-intensive nature of large-scale manufacturing and installation. Within a VRFB system, the Ion-Exchange Membrane (IEM) take up a central role in the system and within the cell stack, as it enables the movement of ions from the anode to the cathode, while maintaining a barrier to prevent unwanted intermixing between the positive and negative electrolytes [5]. Most traditionally, VRFBs have used perfluorosulfonic acid polymers as their most preferred membrane materials, with Dupont's Nafion being particularly renowned for its exceptional chemical stability and high proton conductivity. Although it has good properties, it also carries negative limitations such as high application cost, negative environmental impact during fluorination and small ion selectivity of these ion-exchange membranes have impacted their use in a negative way in applications and commercialization of VRFBs [6]. To address this challenge and promote commercial usage and applications of VRFBs, there is a pressing need for the design and development of new membrane types that exhibit both low vanadium ion permeability, less environmental negative impact, simplified process and reduced cost [7]. Researchers have already started the movement of exploring alternative materials and methods to fabricate IEMs for VRFBs, such as sulfonation of aromatic polymers and pre-treatment of Polybenzimidazole (PBI) membrane to enhance the proton conductivity.

Polybenzimidazole (PBI) membranes have garnered significant interest in VRFB research due to their unique combination of physicochemical properties, which address critical challenges in energy storage systems. PBI exhibits a high glass transition temperature (>400°C) and thermal decomposition temperature (>500°C), enabling stable operation in high-temperature environments. This property is crucial for VRFBs, which generate heat during high-current operation. [8] demonstrated that PBI-based membranes maintain structural integrity at elevated temperatures, preventing performance degradation during prolonged cycling. PBI is highly resistant to acidic and oxidative environments, making it ideal for VRFBs that use strongly acidic electrolytes (e.g., 2–5 M $H_2SO_4$). Its aromatic heterocyclic structure resists hydrolysis and radical-induced degradation. [14] reported that PBI membranes show negligible weight loss even after prolonged exposure to $VO^{2+}/H_2SO_4$ solutions, unlike conventional Nafion® membranes. PBI's dense polymer matrix restricts the crossover of vanadium ions ($VO^{2+}$, $V^{3+}$), reducing self-discharge and capacity decay. This results in a high ion selectivity ($H^+/VO^{2+}$), a critical metric for VRFB efficiency. [9] found that PBI membranes achieved ion selectivity values 3–5× higher than Nafion® 212, significantly improving Coulombic efficiency (98% vs. 93%). PBI membranes possess high tensile strength (80–120 MPa) and flexibility, ensuring durability under the mechanical stresses of flowing electrolytes and stack assembly. A lifecycle analysis by [10] projected a 30% cost reduction for PBI-based VRFBs over a 10-year period. PBI's durability minimizes material waste, and its efficiency reduces energy losses, aligning with circular economy principles. SPEEK membranes have emerged as a very promising alternative to perfluorinated membranes like Nafion® in VRFBs due to their unique positive physicochemical properties. SPEEK exhibits proton conductivity comparable to Nafion®, achieved through the introduction of sulfonic acid ($-SO_3H$) groups during sulfonation. The degree of sulfonation (DS) can be tailored to optimize conductivity while balancing mechanical stability. The development of high-performance membranes for vanadium redox flow batteries (VRFBs) requires balancing proton conductivity, ion selectivity, and mechanical or thermal stability. PBI and SPEEK exhibit complementary properties. with PBI exhibiting exceptional thermal stability (Tg>400∘C), mechanical robustness (tensile strength >80 MPa>80MPa), and chemical resistance to acidic/oxidative environments. However, its low proton conductivity ($10^{-3}$–$10^{-2}$ S $cm^{-1}10^{-3}$–$10^{-2}$S $cm^{-1}$) limits standalone use, and SPEEK exhibit High proton conductivity ($10^{-2}$–$10^{-1}$ S $cm^{-1}10^{-2}$–$10^{-1}$S $cm^{-1}$) via sulfonic acid groups but suffers from excessive swelling at high hydration and reduced mechanical stability. By blending SPEEK into a PBI matrix, we look to synergize, PBI's stability to anchor the membrane structure combining with SPEEK's proton-conducting networks to enhance ionic mobility [11].

In this study, PBI-SPEEK/X composite membranes were fabricated with SPEEK loadings of 3 wt%, 5 wt%, and 10 wt%, doped with phosphoric acid, and evaluated for electrochemical stability and membrane performance in an acidic VRFB relevant environment. Characterization techniques which include Swelling Ratio (SR), Linear Polarization Corrosion Testing and EIS testing using Nyquist plots to also calculate proton conductivity was used to assess and analyse swelling ability and oxidative resistance. Strong emphasis was placed on electrochemical durability, as membranes must be able to endure highly corrosive and acidic vanadium electrolytes without deteriorating and maintain high proton conductivity. The purpose of this research was to establish a electrochemically stable, fire-resistant, cost-effective, and high-performance alternative to Nafion membranes for scalable and safe energy storage systems.

## 2 Methodology and characterizations

### 1.1 Methodology

### *2.1.1 Materials used*

PBI was obtained in polymer membrane form and was sourced from PBI Performance Products, Inc., located in Charlotte, North Carolina, USA. The material, marketed under the trade name Celazole®, was specifically chosen due to its exceptional mechanical, thermal, and chemical resistance properties, making it highly suitable for membrane applications in VRFBs, and used as the primary base polymer. The Polyether Ether Ketone (PEEK) Micron Powder used in your experimental work was sourced from Nanografi in Turkey, with a purity level of 99.95+%. The powder has a particle size of less than 325 mesh, making it ideal for high surface area reactions such as sulfonation. Additional materials included concentrated sulfuric acid (95–98% $H_2SO_4$), Dimethylformamide (DMF) as the solvent, and analytical-grade phosphoric acid ($H_3PO_4$) used for doping. Deionized water was employed for all cleaning and dilution procedures.

### *2.1.2 Sulfonation of PEEK powder to fabricate SPEEK membrane*

5 g of PEEK was gradually added to 50 mL sulfuric acid (98 wt %) in a three-necked round-bottomed flask. The flask was fitted with a mechanical stirrer and a condenser. The reaction mixture was heated in an oil bath to the desired 70 °C sulfonation temperature for the desired time while being continuously stirred. The dissolved PEEK was a dark red, highly viscous solution. The PEEK was sulfonated at 70 °C for reaction times of 6 hours. The sulfonation reaction was terminated by precipitating the polymer in ice-cold water. The precipitated SPEEK formed white noodle-like strands, these were soaked in deionised water overnight and washed until the pH was neutral. The SPEEK polymer was then poured onto a glass Petri dish for uniformity and ease of blending with the PBI membrane. The SPEEK polymer was dried at room temperature overnight and then in a vacuum oven at 60 °C for 24 h.

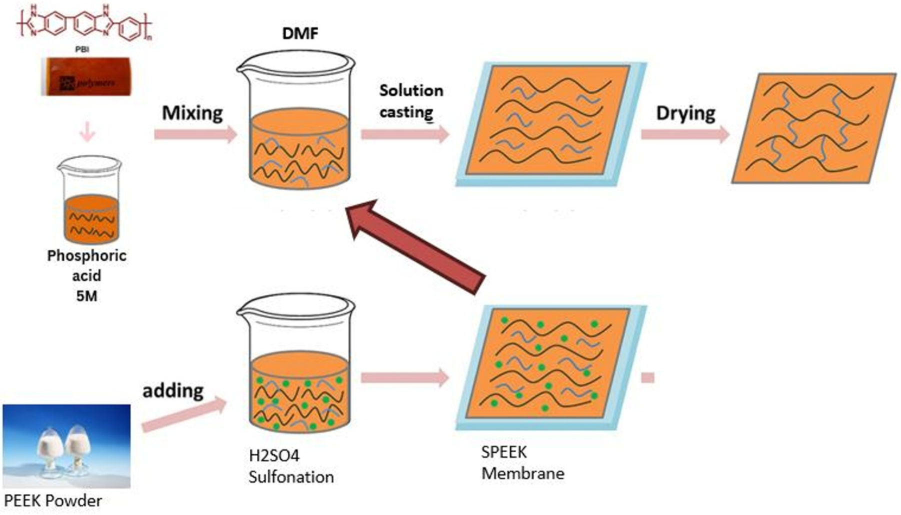

**Fig. 1.** Schematic diagram of the PBI pretreatment, SPEEK preparation and composite membrane fabrication via solution casting.

### *2.1.3 Pretreatment of PBI membrane in phosphoric acid*

The membranes to be employed in this study are about 65 ± 4µm thick PBI membranes, which will be used in as-received conditions. 4 samples of PBI Membranes with fixed dimensions (8 cm × 8 cm) were doped with phosphoric acid at a concentration of 5 M for 72 hours at ambient temperature. After the doping process, thorough cleaning of the doped membranes was therefore conducted, using filter paper to meticulously remove any surplus phosphoric acid residue present on the membrane's surface. This step is considered pivotal and must be completed before advancing to the subsequent stages, such as swelling assessment and thickness measurements. Subsequently, the phosphoric acid-doped membranes will be submerged in a 2.5M sulfuric acid solution. This immersion serves the purpose of promoting the substitution of phosphoric acid with sulfuric acid within the membrane. Following the removal of excess sulfuric acid from the membrane's surface, precise measurements of thickness, swelling ratio and sulfuric acid uptake will be conducted.

These measurements hold significant importance as they serve as crucial parameters before deploying the membranes as separators in VRFBs. To maintain measurement precision, the doped membranes underwent another round of careful wiping with filter paper to eliminate any lingering traces of phosphoric acid from the surface before proceeding with thickness assessments and swelling.

### *2.1.4 PBI/SPEEK-X membrane fabrication*

Composite membranes labelled as PBI/SPEEK-X were fabricated using the solution casting method shown in Table 1. The variable "X" denotes the practical weight ratio of SPEEK to PBI, ranging from 3wt.%, 5wt% and 10wt% named (3MA, 5MA, 10MA) respectfully. Both PBI and SPEEK membranes were prepared using the same procedure. Initially, PBI and SPEEK were dissolved in 20ml of DMF for 6 hours, creating a solution where the PBI did not completely dissolve and SPEEK was completely dissolved.

**Table 1.** Preparation of PBI/SPEEK-X composite membrane via solution casting.

| **Tests** | **Bath 1** | **Bath 2** | **Bath 3** |
|---|---|---|---|
| DMF | 50ml | 50ml | 50ml |
| $H_2SO_4$ | 1M | 1M | 1M |
| PBI | 0.2692g | 0.2692g | 0.2692g |
| SPEEK | 3wt% | 5wt% | 10wt% |

The resulting solution was then poured into a glass mould. After casting, the solution-filled mould was subjected to evaporation at 80°C for a duration of 24 hours. Subsequently, the solidified solution-cast membranes were carefully peeled off with the use of deionized water. Before utilization, the PBI-SPEEK/X membranes shown in Table 2 all underwent a soaking process in a 1M $H_2SO_4$ solution for a period of 24 hours to prepare them for characterization.

Table 2. Sample identification and representation for all 5 samples.

| **Sample Identity** | **Sample name** |
|---|---|
| Base PBI membrane | Pure PBI |
| SPEEK Membrane | SPEEK base membrane |
| 3wt% SPEEK into PBI base | 3M A |
| 5wt% SPEEK into PBI base | 5M A |
| 10wt% SPEEK into PBI base | 10M A |

## 2.2, Characterizations of PBI/SPEEK-X blended membranes

### *2.2.1 Acid uptake measurements*

The acid uptake is related to the swelling ratio and membrane thickness. The acid uptake was assessed before and after immersion in sulfuric and phosphoric acids, which are essential in the context of VRFBs and were used in the study for pretreatment and sulfonation purposes. The swelling ratio is determined by measuring the dimensions of the dry membrane and comparing them to the dimensions after immersion in the acid solutions.

$$AU\% = \left(\frac{m_{wet} - m_{dry}}{m_{dry}}\right) \text{x } 100 \tag{1}$$

AU is the acid uptake, $m_{wet}$ is the wet weight of the membrane (g), $m_{dry}$ is the dry weight of the membrane (g). Acid uptake characterization is a crucial and critical step in evaluating the performance and functionalization of PBI-SPEEK blended membranes, especially when doped with phosphoric acid and sulfuric acid. Acid uptake directly influences the membrane's proton conductivity, ionic mobility, and degree of protonation, which are all essential and highly important parameters for efficient operation in VRFBs [10]. Higher acid uptake typically relates to an increased number of proton-conducting sites, facilitating improved ionic transport via the Grotthuss mechanism [12]. However, excessive acid uptake can also compromise mechanical strength and dimensional stability, leading to swelling and potential degradation under operational conditions. It is therefore important to optimize acid uptake for balancing conductivity and structural integrity, ensuring lasting membrane durability in highly acidic VRFBs [12].

### *2.2.2 Potentiodynamic linear polarization*

The experiments were conducted using a Potentiostat/galvanostat in Figure 2 integrated with a three-electrode corrosion cell. The setup consisted of, a membrane sample clamped into a custom-made Teflon holder acting as the working electrode (WE), A platinum counter electrode (CE), and A Saturated Calomel Electrode (SCE) as the reference electrode (RE). The electrolyte solution used was 1 M sulfuric acid, simulating real VRFB operating conditions. It was also of vital importance to run these tests because the goal was to establish the corrosion potential of all 5 samples that would help analyze the proton conductivity and ionic resistance.

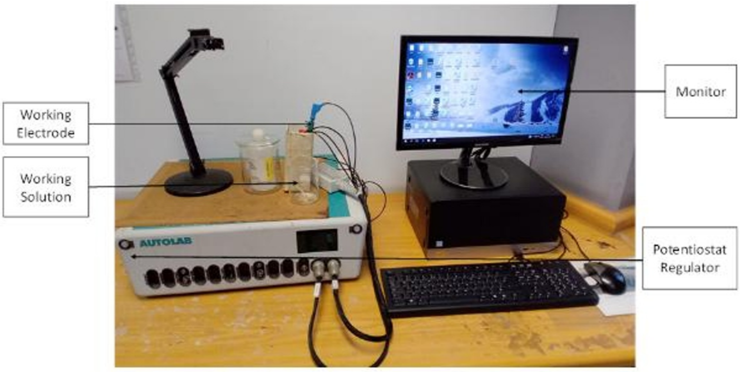

**Fig. 2.** The Potentiodynamic polarization process.

It is essential that membrane materials must exhibit excellent chemical stability to ensure sustained and efficient performance. Linear polarization testing allows for the measurement of corrosion current density (I_corr) and corrosion potential (E_corr), which are crucial indicators of a membrane's resistance to oxidative degradation and electrochemical corrosion [13].

EIS was then used to evaluate the proton conductivity of the membranes via Nyquist plots, which display the imaginary component (Z'') versus the real component (Z') of the impedance. The arc radius of each Nyquist plot corresponds to the bulk resistance (R) of the membrane.

The proton conductivity (σ) was calculated using the formula:

$$\sigma = \frac{L}{R\ x\ A} \tag{2}$$

Where:

- **L** = membrane thickness = 0.01 cm
- A = membrane area = 1.77 cm² (for a 1.5 cm diameter circular membrane)
- R= bulk resistance of the membrane

# 3 Results and discussions

## 3.1 Acid uptake measurements

The swelling ratio is displayed in Figure 3. The graph shows the acid uptake of the membranes, which is a key factor influencing proton conductivity and mechanical stability. In VRFBs, membranes require sufficient hydration to facilitate proton transport while avoiding excessive swelling that could compromise structural integrity. Achieving an optimal swelling ratio is critical for balancing ionic transport with physical durability. The results showed that the swelling ratio increased with the acid concentration and higher swelling ratios enhanced the proton conductivity essential for ion transport in VRFBs, also observed by Divya et al. [14].

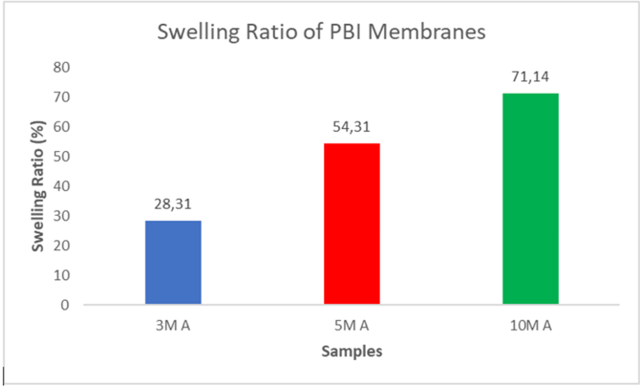

**Fig. 3.** Swelling ratio of PBI membrane.

PBI membrane had a dry Membrane Mass of 0.2692 g. using the acid uptake equation:

$$AU\% = \left(\frac{m_{wet} - m_{dry}}{m_{dry}}\right) X\ 100 \tag{3}$$

$$AU\% = \left(\frac{0.3454_{wet} - 0.2692_{dry}}{0.2692_{dry}}\right) X\ 100$$
$$(3M\ A)\ \boldsymbol{AU}\% = \mathbf{28.31}\% \tag{4}$$

$$AU\% = \left(\frac{0.4154_{wet} - 0.2692_{dry}}{0.2692_{dry}}\right) X\ 100$$
$$(5M\ A)\ AU\% = \mathbf{54.31}\% \tag{5}$$

$$AU\% = \left(\frac{0.4607_{wet} - 0.2692_{dry}}{0.2692_{dry}}\right) X\ 100$$
$$(10M\ A)\ AU\% = \mathbf{71.14}\% \tag{6}$$

The swelling ratio was higher with SPEEK content, due to a characteristic of hydrophilicity of sulfonic acid groups introduced by SPEEK. 3M A exhibited the lowest swelling at 28.31%, indicating low hydration for efficient proton conduction. 5M A had a moderate swelling ratio at 54.31%, indicating sufficient hydration without compromising structural stability. 10M A exhibited the highest swelling and acid uptake at 71.14%, which was too high and would lead to membrane deterioration and reduced ion selectivity. The 5M A membrane possesses the ideal balance, with its swelling ratio creating the necessary hydration for higher proton conductivity without sacrificing mechanical stability. Furthermore, the swelling ratio influences the membrane pores which affects the vanadium ion crossover. 3M A is mechanically stable but may lack sufficient ionic mobility for conduction properly due to limited hydration and has a low crossover risk. 10M A, with a high swelling ratio, can contribute towards structural deformation as well as higher vanadium ion crossover, minimizing and reducing membrane lifetime. Increased SPEEK content incorporates more sulfonic acid functional groups, which are acid-absorbing and facilitate proton conduction. SPEEK (10 wt%) 10M A, leading to excessive swelling and phase separation. All these results confirm directly the conclusion that 5M A presents a proper composition for SPEEK-PBI membranes for VRFB application with equilibrium and a balance between hydration, proton selectivity, and low vanadium permeability.

### 3.2 Linear polarization corrosion testing

The linear polarization curves shown in Figure 4 give essential insight into the electrochemical behaviour of the base samples and the fabricated membrane samples when exposed to acidic environments typical of VRFB battery systems.

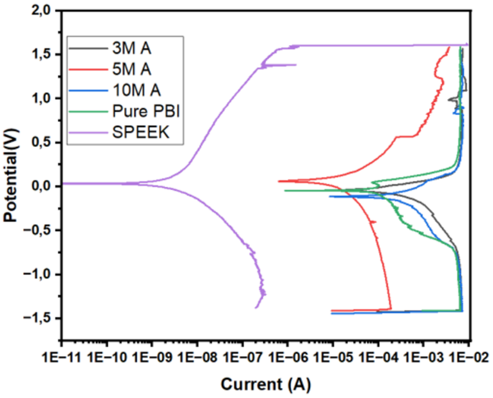

**Fig. 4.** Potentiodynamic polarization curves of the membranes.

The corrosion potential (Ecorr) provides insight into the thermodynamic stability of the membranes against corrosion and also gives us the potentials of all the samples. From the polarization curves among the five tested membranes, SPEEK, Pure PBI, and PBI blended with 3 wt%, 5 wt%, and 10 wt% SPEEK (3M A, 5M A, 10M A respectively), it was observed that SPEEK has a potential (Ecorr) =0.05 V, signifying good corrosion resistance, which can be attributed to its strong sulfonated structure. Pure PBI, known for its aromatic benzimidazole backbone, offered low corrosion resistance (Ecorr) = -0.090 V less than SPEEK. Among the modified membranes, the 5M A membrane exhibits the highest (Ecorr) =0.1 V, suggesting enhanced stability compared to 3M A = 0.06 V and 10M A = 0.048 V.

The corrosion current density (Icorr) is also a very important parameter to analyze, representing the rate of corrosion. The lower the Icorr value, this indicates reduced corrosion rates and enhanced longevity of the membrane. From Figure 4, we observed Icorr values for the samples as follows SPEEK= ~$10^{-6}$ A/cm², Pure PBI= ~$10^{-4}$ A/cm², 3M A= ~$10^{-7}$ A/cm², 5M A= ~$10^{-5}$ A/cm², 10M A= ~$10^{-4}$A/cm². The 3M A membrane exhibits the lowest Icorr = ~$10^{-8}$ A/cm², indicating the slowest corrosion rate among all samples. This could be attributed to its moderate SPEEK-PBI blend, which enhances the membrane's protective characteristics. SPEEK shows a relatively high corrosion density despite its high Ecorr, this shows that it is more prone to degradation and deterioration in terms of current density compared to the blended modified membranes. 5M A and 10M A membranes show moderate corrosion densities, confirming their balanced electrochemical stability. Pure PBI has an Icorr of ~$10^{-4}$ A/cm², indicating relatively high corrosion vulnerability when compared to the blended modified membranes, so indicating the need for a pretreatment doping of the PBI membrane in phosphoric acid.

It was necessary to have a comparative analysis for both current potential Ecorr and corrosion current density Icorr for all 5 samples involved. The comparative analysis and observations revealed and showed that the incorporation and blending of the SPEEK membrane into the PBI membrane improves the membrane corrosion resistance to some extent. The 5 M A membrane was observed and demonstrates the best performance overall, with a low corrosion current density. This balance suggests and indicates that it is suitable for prolonged use in VRFB systems. However, the 3 M A membrane also showcases a good performance as one of the best candidates alongside 5M A for both corrosion potential and current density, as it combines reasonable stability with low corrosion current density. Comparatively, the SPEEK membrane has good corrosion resistance, but higher corrosion current density. This therefore indicates faster degradation. Pure PBI, on the other hand, lacks sufficient resistance to corrosion and Icorr = ~$10^{-4}$ A/cm². The results and comparative analysis suggest that the 5M A membrane offers the best compromise between electrochemical stability and corrosion resistance, highlighting and making it the most suitable candidate for VRFB applications. The 3M A membrane, with its exceptionally low Icorr, can also be considered for applications requiring low current leakage. SPEEK, while resistant to corrosion, may require additional stabilization measures to mitigate degradation during prolonged battery cycling. Pure PBI therefore indicates and supports that pretreatment in phosphoric acid is paramount for it to have a more balanced electrochemical performance This linear polarization corrosion tests and analysis demonstrate the importance of optimizing SPEEK-PBI blends to enhance membrane properties for electrochemical performance in VRFB systems and applications. Among the tested membranes, the 5M A composition emerges as the best candidate, followed by 3M A, followed by the SPEEK membrane, Followed by the PBI membrane and lastly the 10M A membrane.

### 3.3 Electrochemical impedance spectroscopy (EIS) Testing

EIS was used to evaluate the proton conductivity of the membranes via Nyquist plots, which display the imaginary component (Z") versus the real component (Z') of the impedance. As seen in the Figure 5 (A–E), the arc radius of each Nyquist plot corresponds to the bulk resistance (R) of the membrane.

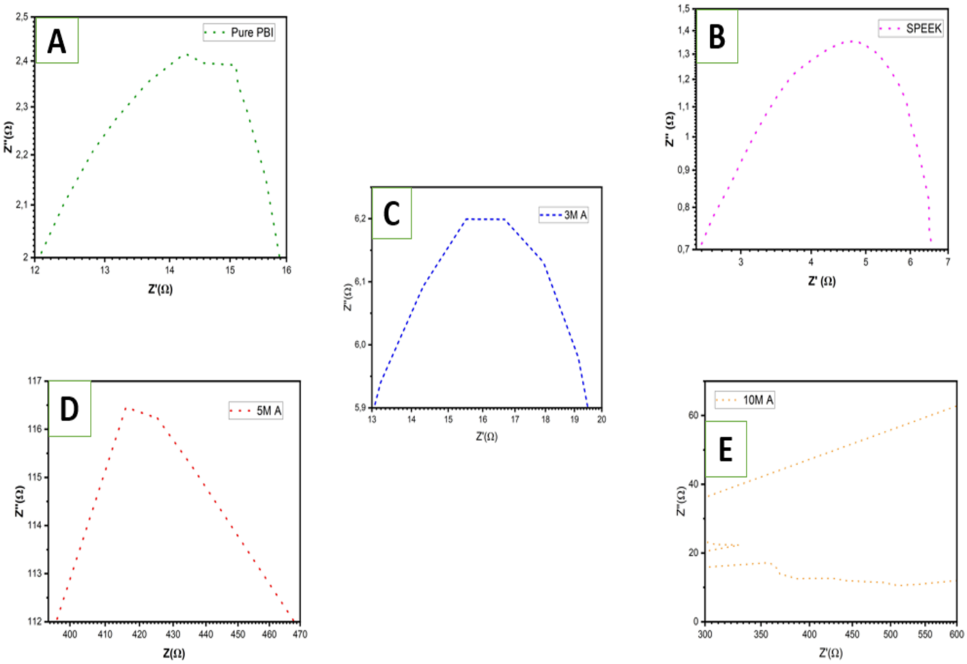

**Fig. 5**. EIS results for PBI/SPEEK-X membrane for proton conductivity analysis.

Pure PBI represented by Figure 5(A), exhibited a high resistance with Z' intercept around 13 Ω and a small semicircle, indicative of limited ionic mobility due to the lack of sulfonic acid groups. SPEEK represented by Figure 5(B), showed a lower resistance ~3.5 Ω, confirming the influence of sulfonic acid groups that promote proton transport. 3M A (3wt% SPEEK-PBI) represented by Figure 5(C), had a moderate arc and resistance ~16 Ω, suggesting partial improvement in conductivity. 5M A (5wt% SPEEK-PBI) represented by Figure 5(D), displayed the smallest arc ~415–470 Ω in the high-frequency region, corresponding to the lowest membrane resistance and thus the highest conductivity. 10M A (10wt% SPEEK-PBI) represented by Figure 5(E), showed an irregular arc shape and higher resistance ~580 Ω, indicative of potential phase separation and reduced proton transport efficiency despite higher sulfonic content. As seen in the Figure 5(A–E), the arc radius of each Nyquist plot corresponds to the bulk resistance (R) of the membrane.

- Pure PBI (Figure A): Intercept at Z' ≈ 13.0 Ω
- SPEEK (Figure B): Intercept at Z' ≈ 3.5 Ω
- 3M A (3wt% SPEEK-PBI) (Figure C): Intercept at Z' ≈ 16.0 Ω
- 5M A (5wt% SPEEK-PBI) (Figure D): Intercept at Z' ≈ 415.0 Ω
- 10M A (10wt% SPEEK-PBI) (Figure E): Intercept at Z' ≈ 580.0 Ω

The proton conductivity (σ) was calculated using the formula:

$$\sigma = \frac{L}{R\ x\ A} \tag{7}$$

Where:

- **L** = membrane thickness = 0.01 cm
- A = membrane area = 1.77 cm² (for a 1.5 cm diameter circular membrane)
- R= bulk resistance of the membrane

$$\sigma = \frac{0.01}{13\ x\ 1.77} \tag{8}$$

$$\sigma = 0.00044\frac{S}{cm} = 0.44mS/cm \tag{9}$$

$$\sigma = \frac{0.01}{3.5\ x\ 1.77} \tag{10}$$

$$\sigma = 0.00161\frac{S}{cm} = 1.61mS/cm \tag{11}$$

$$\sigma = \frac{0.01}{16\ x\ 1.77} \tag{12}$$

$$\sigma = 0.00036\frac{S}{cm} = 0.36mS/cm \tag{13}$$

$$\sigma = \frac{0.01}{415\ x\ 1.77} \tag{14}$$

$$\sigma = 0.0000136\frac{S}{cm} = 0.0136\ mS/cm \tag{15}$$

$$\sigma = \frac{0.01}{580\ x\ 1.77} \tag{16}$$

$$\sigma = 0.0000097 \frac{S}{cm} = 0.0097\ mS/cm \tag{17}$$

The proton conductivity values obtained reflect the influence of both the membrane composition and the distribution of sulfonic acid groups. SPEEK, being highly sulfonated, displayed the highest conductivity= 1.61 mS/cm, attributed to its abundant -$SO_3H$ groups which provide effective proton transport channels. However, its low mechanical and oxidative stability limits its standalone application in VRFB systems.

Pure PBI showed modest conductivity= 0.44 mS/cm, benefiting from its dense, stable structure but suffering from the absence of intrinsic proton-conducting groups. The 3M A (3wt% SPEEK-PBI) blend exhibited slightly lower conductivity= 0.36 mS/cm, suggesting that while low level SPEEK integration introduces proton conduction pathways, the extent of blending is insufficient for high performance. The 5M A (5wt% SPEEK-PBI) membrane, exhibited low proton conductivity= 0.0136 mS/cm, however this 5M A (5wt% SPEEK-PBI) has been demonstrated to achieve optimal performance when considering the overall balance between conductivity, thermal stability, and corrosion resistance. The high resistance in this sample may be due to membrane compaction or measurement specific issues such as increased thickness or improper electrode contact. The 10M A (10wt% SPEEK-PBI) membrane, with the lowest measured conductivity= 0.0097 mS/cm, indicates that excessive SPEEK loading may cause phase segregation, poor dispersion, and disrupted proton channels. The EIS results suggest that there is an optimal SPEEK content that balances ionic conductivity with morphological and electrochemical stability.

## 4 Conclusion

This study produced PBI membranes by blending with SPEEK, aiming to create a more electrochemically stable, robust and cost-effective alternative membrane to Nafion for VRFBs. This study is part of a larger study that looked at the physical, chemical, thermal and electrochemical behaviour of this PBI-SPEEK/X solution casted membranes. The swelling ratio of the membranes increased significantly, which implies that there is an increase in water uptake and protonation. The 5M A showed a more balanced performance with a moderate swelling ratio necessary for the VRFBs, low vanadium ion crossover, and good dimensional and mechanical stability. Among all samples, the 5 MA (5wt% SPEEK-PBI) blends also exhibited the most favourable corrosion profile, with a high corrosion potential and a low corrosion current density. Suggesting the membrane has good electrochemical stability, moderate corrosion activity and good conductivity compared with other membranes. The 5M A membrane has a low proton conductivity compared to SPEEK and PBI membranes which can be attributed to membrane compaction or measurement specific issues such as increased thickness or improper electrode contact. Overall, having looked at the acid uptake which influences vanadium ion crossover, linear polarization corrosion testing which gave us insight on thermodynamic stability of membranes against corrosion and also corrosion current density which gave insight on the rate of corrosion, and lastly the EIS tests which gave us the resistance of the membranes which helped us calculate for proton conductivity. Through them all, the 5M A (5wt% SPEEK-PBI) portrayed more balanced results but low proton conductivity, thus making SPEEK and PBI very close in terms of preference, having only looked at the electrochemical behaviour of the membranes. The results performance can be represented in this way, 5M A > SPEEK>PBI>3M A>10M A

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