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COMPARATIVE CHARACTERIZATION OF PROTON EXCHANGE MEMBRANES BY IMPEDANCE SPECTROSCOPY

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ABSTRACT

This study presents an electrochemical impedance spectroscopy (EIS) analysis of proton exchange nanocomposite membranes (NDK) in compari-son with commercial Nafion 117 under fully hydrated conditions. The im-pedance spectra were recorded in the frequency range from 1 MHz to 0.01 Hz using a low AC amplitude (5–10 mV) at room temperature. The Nyquist plots revealed characteristic features of membrane bulk resistance (Rb), bulk capacitance (Cb), and interfacial constant phase element (CPE) behavior.

The impedance response demonstrated a small semicircle in the high-frequency region, associated with bulk dielectric relaxation, and an inclined low-frequency line corresponding to interfacial polarization effects modeled by a constant phase element. Although Nafion 117 showed lower bulk re-sistance due to its well-developed phase-separated hydrophilic channels and high density of sulfonic acid groups, the NDK membrane exhibited compa-rable proton transport properties while offering improved ion selectivity. The results confirm that electrochemical impedance spectroscopy effectively dis-tinguishes bulk and interfacial processes in proton exchange membranes and demonstrates the potential of NDK nanocomposite membranes as promising cost-effective alternatives for fuel cell and electrochemical energy applications.

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Introduction

Proton exchange membranes (PEMs) play a crucial role in electrochemical energy conversion and storage systems, particularly in proton exchange membrane fuel cells (PEMFCs), water electrolyzers, and redox flow batteries [1]. The primary function of a PEM is to selectively conduct protons (H^+) while acting as an electronic insulator and preventing the crossover of fuel or other ionic species. In practical systems, the membrane serves simultaneously as an electrolyte and as a physical separator between the anode and cathode compartments, ensuring charge balance while maintaining chemical isolation of reactants. Efficient proton transport across the membrane is essential for sustaining current flow and minimizing internal resistance losses. Therefore, the efficiency, durability, and overall performance of such electrochemical devices are strongly dependent on the physicochemical and electrochemical properties of the membrane material [2]. Parameters such as proton conductivity, ion exchange capacity, water uptake, thermal stability, mechanical strength, and chemical resistance directly influence device efficiency and long-term stability.

Among commercially available membranes, Nafion 117 remains the most widely used benchmark material due to its high proton conductivity, chemical stability, and well-developed phase-separated morphology consisting of hydrophobic polymer backbones and hydrophilic sulfonic acid domains [3]. Upon hydration, these hydrophilic domains form interconnected proton-conducting channels that enable efficient proton transport via vehicular and Grotthuss mechanisms. This unique nanophase-separated structure provides Nafion with excellent ionic conductivity under fully hydrated conditions. However, Nafion membranes are expensive and may suffer from excessive swelling, fuel crossover, and limited ion selectivity in certain applications [4–5]. These limitations have motivated extensive research efforts toward the development of alternative hydrocarbon-based and nanocomposite proton exchange membranes that offer improved cost-effectiveness, controlled swelling behavior, enhanced mechanical robustness, and tailored ion transport properties suitable for next-generation electrochemical energy systems.Nanocomposite membranes incorporating inorganic fillers such as SiO_2 or other nanostructured additives have attracted considerable attention due to their potential to enhance mechanical stability, control swelling behavior, and improve ion selectivity without severely compromising proton conductivity [6-7]. The introduction of nanoscale fillers can modify membrane morphology, regulate water retention, and influence proton transport pathways. However, a comprehensive understanding of bulk and interfacial transport phenomena in such membranes is essential for optimizing their performance.

Electrochemical impedance spectroscopy (EIS) is a powerful and non-destructive technique widely used to investigate ion transport, dielectric relaxation, and interfacial polarization processes in proton exchange membranes [8-9]. By analyzing the real (Z') and imaginary (Z'') components of complex impedance over a broad frequency range, it is possible to separate bulk membrane resistance, capacitive behavior, and electrode–membrane interfacial effects. Nyquist plots provide valuable insight into membrane bulk resistance (Rb), bulk capacitance (Cb), and non-ideal interfacial behavior typically modeled using constant phase elements (CPE) [10-11]. These parameters are directly related to proton conductivity and structural characteristics of the membrane.

In this study, a comparative electrochemical impedance analysis of a proton exchange nanocomposite membrane [12] (PEM) synthesized in our previous work and commercial Nafion 117 was performed under fully hydrated conditions. The aim of the study was to evaluate the bulk resistivity, dielectric properties, and interface polarization, as well as determine the proton conductivity using equivalent circuit modeling. The results provide insight into the transport mechanisms within the membranes and assess the potential of NDK membranes as a cost-effective alternative for electrochemical energy applications.

Experimental

Proton exchange nanocomposite membranes (PEMs) were synthesized by solution casting using a sulfonated polymer matrix combined with inorganic nanofillers. The synthesis process of the nanocomposite membrane is described in detail in our work [13]. Commercial Nafion 117 membrane (thickness ≈172 μm) was utilized as a benchmark reference material, while the prepared NDK membrane exhibited an average thickness of approximately 142 μm, determined using a calibrated digital micrometer.

We have prepared a symmetrical two-electrode blocking device (fig 1.) for impedance characterization, with an image of the cell (left) and a schematic representation (right). The membrane sample is placed within a defined aperture (~4 cm^2 effective area) and is sandwiched between polished copper electrodes placed in an electrically insulating frame. Uniform mechanical clamping is used to ensure the stability of the electrode-membrane interface and minimize surface resistance artifacts. The symmetrical blocking configuration suppresses Faradaic charge transfer processes, allowing for the isolation of bulk ionic conductivity and surface polarization responses. This geometry allows for reliable extraction of bulk resistivity and dielectric relaxation parameters in a wide frequency range under fully hydrated conditions.

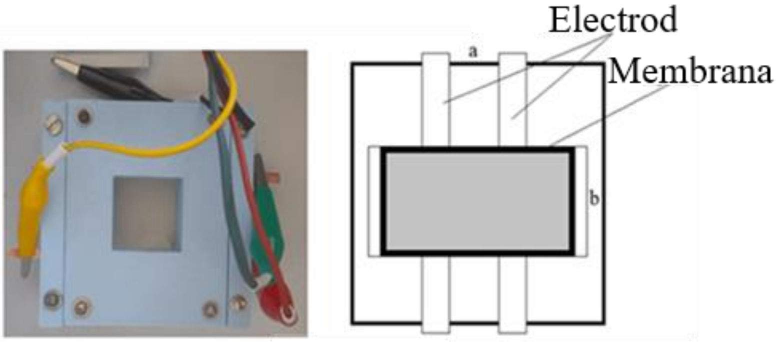

Figure 1. *Impedance measuring devices*

Photograph (left) and schematic representation (right) of the symmetric two-electrode blocking cell employed for impedance characterization. The membrane sample is positioned within a defined aperture (~4 cm² effective area) and sandwiched between polished copper electrodes housed in an electrically insulating frame. Uniform mechanical compression is applied to ensure stable electrode–membrane contact and minimize interfacial resistance artifacts.

Impedance spectroscopy of the membranes was carried out on a potentiostat/galvonastat Model: CS350M (China). The symmetric blocking configuration suppresses Faradaic charge transfer processes, enabling isolation of bulk ionic conduction and interfacial polarization responses. This geometry allows reliable extraction of bulk resistance and dielectric relaxation parameters across a broad frequency window (1 MHz–0.01 Hz) under fully hydrated conditions.

Prior to impedance measurements, all membranes were converted into the proton (H^+) form and conditioned under fully hydrated conditions. Nafion 117 membranes underwent a standard purification and protonation procedure consisting of sequential immersion in 3% hydrogen peroxide solution at approximately 100 °C for 30 minutes to remove organic contaminants, boiling deionized water rinsing, treatment in 2 M hydrochloric acid at ~100 °C for 30 minutes to ensure complete proton exchange, and final washing in boiling deionized water until neutral pH was achieved. The membranes were then stored in deionized water until characterization was determined. The NDK membranes were thoroughly rinsed and equilibrated in deionized water for at least 24 hours prior to testing to ensure complete hydration and stability of the ionic domains. The membranes were then acid-treated with 1 M sulfuric acid for 24 hours to perform the measurements. Electrochemical impedance spectroscopy (EIS) measurements were performed using a potentiostat/impedance analyzer under fully humidified conditions at ambient temperature (≈25 °C). The membrane samples were placed between two blocking copper (Cu) electrodes in a symmetrical configuration. The effective electrode area was kept constant for all measurements. A controlled mechanical clamping system was employed to ensure uniform electrode contact and minimize interfacial contact resistance. Impedance spectra were recorded over a broad frequency range from 1 MHz to 0.01 Hz using a small-amplitude sinusoidal perturbation (5–10 mV) to guarantee linear response behavior and avoid non-linear polarization effects. The complex impedance response was analyzed in terms of its real (Z') and imaginary (Z'') components, and Nyquist plots were constructed accordingly. The experimental spectra were fitted using complex nonlinear least-squares (CNLS) regression to an equivalent electrical circuit model comprising bulk membrane resistance (Rb) in parallel with bulk capacitance (Cb), combined in series with a constant phase element (CPE) to account for non-ideal interfacial polarization phenomena [11].

The impedance of the CPE was defined as:

$$Z_{CPE} = \frac{1}{Q(j\omega)^n} \qquad (1)$$

where Q represents the CPE coefficient, ω is the angular frequency, j is the imaginary unit, and n ($0 < n < 1$) reflects deviation from ideal capacitive behavior due to structural heterogeneity or distributed relaxation processes.

The bulk resistance (Rb) was extracted from the high-frequency intercept of the Nyquist plot with the real axis. Proton conductivity (σ) was calculated according to

$$\delta = \frac{L}{R_b \cdot A} \qquad (2)$$

where L denotes membrane thickness and A corresponds to the effective electrode area. Each measurement was performed in triplicate to ensure reproducibility, and fitting quality was assessed based on chi-square (χ^2) error values and residual distribution analysis.

Throughout all measurements, membranes were maintained under fully hydrated conditions to eliminate dehydration effects and ensure reliable evaluation of intrinsic proton transport properties.

Results and Discussion

To provide insight into the nanocomposite nature of the NDK membrane, a scanning electron microscope (SEM) image of its surface morphology was presented. The obtained micrographs show that the membrane surface is relatively uniform and continuous, indicating the formation of a well-developed polymer film. At low magnification (38×), no visible macro-defects such as cracks, voids, or large pores are observed, indicating the good structural integrity and film-forming ability of the polymer matrix.

The SEM image also shows the presence of finely dispersed particles distributed along the membrane surface. These features can be attributed to the incorporation of inorganic nano-fillers such as SiO_2 nanoparticles and carbon nanotubes into the polymer matrix, confirming the nanocomposite nature of the membrane. The relatively uniform distribution of these nano-fillers indicates good interface compatibility between the organic polymer phase and the inorganic components. Such compatibility is crucial for achieving improved physicochemical properties in nanocomposite membranes.

Although some local agglomeration of nanoparticles is observed in some regions, this phenomenon does not significantly compromise the overall structural uniformity. On the contrary, the presence of nanofillers contributes to the densification of the membrane structure by reducing the free volume within the polymer matrix. This structural modification is known to improve ion selectivity and suppress the cross-linking of unwanted species, which is especially important for electrochemical energy systems.

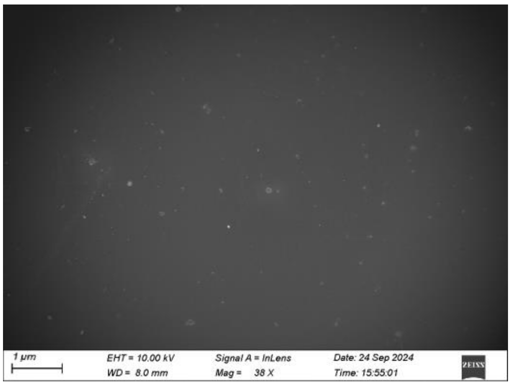

Figure 3. *SEEM image of NDK nanocomposite membrane*

Furthermore, the incorporation of inorganic nanofillers into polymer matrices has been widely reported to improve key membrane properties, including proton conductivity, mechanical strength, and chemical stability. In particular, silicon-based nanofillers can improve water retention within the membrane and thereby facilitate proton transport by forming continuous hydrogen-bonded networks. As a result, the nanocomposite structure plays a crucial role in optimizing the transport and barrier properties of the membrane.

Overall, SEM analysis confirms that the NDK membrane exhibits a compact, uniform, and well-integrated nanocomposite structure. The effective dispersion of nanofillers within the polymer matrix indicates the successful fabrication of a nanocomposite membrane-brane, which is expected to enhance its electrochemical performance. These structural features make the NDK membrane a promising candidate for application in advanced energy systems such as redox flow batteries and proton exchange membrane fuel cells.

The calculated proton conductivity values further support this observation. Nafion 117 exhibits conductivity on the order of 10^{-2} $S\cdot cm^{-1}$, consistent with literature values for fully hydrated membranes. The NDK membrane shows slightly lower conductivity, which may be attributed to differences in microphase separation and proton-conducting channel connectivity.

The small semicircular feature observed at high frequencies represents dielectric relaxation associated with the bulk RC response of the membrane. In ideal Debye-type systems, this semicircle would be well-defined; however, in practical membrane systems, it appears compressed due to distributed relaxation times and structural heterogeneity.

In the low-frequency region, both membranes display an inclined linear behavior, deviating from ideal vertical capacitive response. This behavior is characteristic of interfacial polarization effects and is effectively described using a constant phase element (CPE). The deviation from ideal capacitive behavior ($n < 1$) reflects non-uniform charge accumulation at the electrode–membrane interface, surface roughness, and heterogeneity of ionic domains.

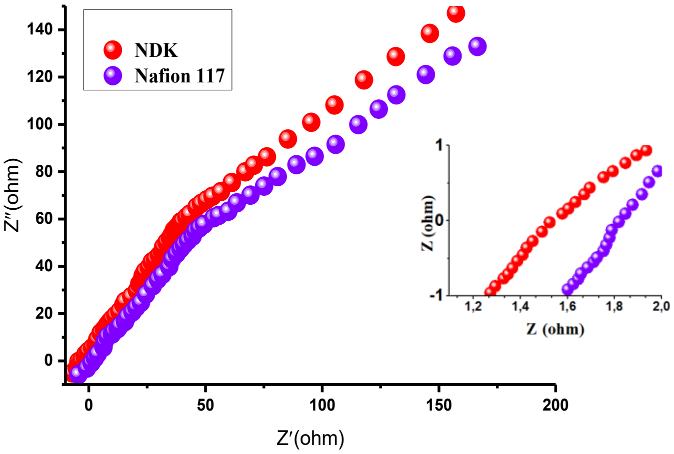

Figure 2. *Nyquist diagram for NDK (red) and Nafion 117 (purple) membranes.*

Interestingly, the NDK membrane exhibits slightly higher Z″ values in the low-frequency domain, suggesting increased interfacial impedance or reduced interfacial capacitance compared to Nafion 117. This may result from differences in surface chemistry, distribution of sulfonic acid groups, or reduced hydration at the membrane–electrode interface.

From a structural perspective, Nafion 117 benefits from its well-defined phase-separated morphology, consisting of hydrophobic PTFE backbones and hydrophilic sulfonic acid clusters. Upon hydration, these clusters form interconnected nanochannels that enable efficient proton transport via both vehicular and Grotthuss mechanisms. In contrast, hydrocarbon-based nanocomposite membranes such as NDK may lack similarly optimized phase segregation, resulting in slightly increased transport resistance.

However, the incorporation of inorganic nanofillers in the NDK membrane provides additional advantages. Nanofillers can enhance mechanical stability, suppress excessive swelling, and improve ion selectivity. Although the overall proton conductivity is marginally lower than that of Nafion 117, the NDK membrane demonstrates competitive performance while potentially offering improved durability and reduced cost.

Overall, the impedance analysis confirms that proton transport in both membranes is governed primarily by bulk ionic conduction under fully hydrated conditions, while interfacial polarization effects become significant at low frequencies.

Table 1

Main electrochemical parameters of membranes

Membrana	**Z\` (Ω) Om**	**Proton conductivity (σ, S·cm-¹)**
Nafion 117	1.3	3.3 × 10-^{3}
NDK	1.6	2.7 × 10-^{3}

The combination of equivalent circuit modeling and Nyquist plot interpretation enables clear differentiation between bulk transport and interfacial processes.

Conclusions

In this study, electrochemical impedance spectroscopy (EIS) was used to study the proton transport behavior of a nanocomposite proton exchange membrane (PEM) under fully sulfuric acid-soaked conditions in comparison with commercial Nafion 117. Impedance analysis interpreted by Nyquist plots and equivalent circuit modeling allowed a clear separation of the membrane's basic resistance, dielectric relaxation processes, and interface polarization phenomena. The basic resistance values were determined from the high-frequency intercept point on the real axis, which gave approximately 1.3 Ω for Nafion 117 and ~1.6 Ω for the PEM membrane. Accordingly, the proton conductivity of Nafion 117 was estimated to be ~3.3×10^{-3} S·cm^{-1}, while the PEM membrane showed a slightly lower conductivity (~2.7×10^{-3} S·cm^{-1} under comparable conditions). The fact that the proton permeability of the membranes here is several times higher than that of hydrated membranes is due to the fact that the membranes are fully converted to an acidic form.

The results showed that Nafion 117 has a lower volume resistivity (1.3 Ω) and consequently a higher proton conductivity (3.3×10^{-3} S·cm^{-1}) due to its high density of sulfo groups. The NDK membrane, on the other hand, showed a slightly higher resistivity (1.6 Ω) and a lower conductivity (2.7×10^{-3} S·cm^{-1}). This difference in conductivity is small, and the NDK membrane shows practically competitive results under the same test conditions. Continuous phase element (CPE) characteristics were observed in both samples, which makes the NDK membrane a viable alternative to the Nafion 117 membrane.

These findings highlight the effectiveness of EIS as a diagnostic tool for distinguishing bulk and interfacial electrochemical processes and provide valuable insight for the further optimization of nanocomposite proton exchange membranes for fuel cell and electrochemical energy applications.

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