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Sol–Gel Fabrication of Hybrid Semi-Interpenetrating Ion-Solvating Membranes by TEOS Crosslinking for Alkaline Electrolyzers

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Abstract. Ion-solvating membranes are an emerging membrane class for alkaline water electrolysis, where hydroxide transport occurs through KOH-solvated pathways rather than fixed cationic groups but achieving high conductivity without excessive swelling and poor oxidative durability remains challenging. Here, we design hybrid semi-interpenetrating xTEOS–PVA:xPVP membranes by combining acid-catalyzed TEOS sol–gel crosslinking with PVA/PVP polymer entanglement, followed by solution casting and KOH activation. FTIR confirms the formation of Si–O–Si and Si–O–C linkages with residual silanols, demonstrating an inorganic network integrated within the polymer matrix. SEM reveals a composition-dependent morphology transitioning from dense polymer films to textured hybrid structures at intermediate TEOS loadings and re-densified surfaces at the highest TEOS contents. This structural evolution governs hydration and transport: water uptake and swelling decrease with TEOS, while hydroxide conductivity shows a step increase upon introducing a small TEOS fraction at high PVP content, reaching ~60 mS cm^{-1} at 25 °C and ~100 mS cm^{-1} at 80 °C in 1 M KOH for the optimal composition (1T-PVA:1.5PVP). Importantly, TEOS incorporation markedly enhances oxidative stability, with ~90% mass retention near the same intermediate composition. The results demonstrate that inorganic sol–gel crosslinking plus polymer semi-interpenetration can generate well-solvated transport pathways without excessive swelling, enabling membranes that combine high OH^- conductivity with improved oxidative durability for alkaline membrane electrolyzers.

Introduction

Alkaline water electrolysis (AWE) is a mature and scalable route to produce high-purity hydrogen using low-carbon electricity [1]. In anion-exchange membrane water electrolysis (AEMWE), a solid polymer electrolyte acts as the ion conductor and separator, enabling more compact cells and simpler operation than conventional liquid KOH systems [2]. A major advantage of alkaline operation is the ability to use earth-abundant based catalysts instead of precious metals, which can reduce cost and supply-chain constraints. Well-designed membranes can also limit gas crossover and support high efficiency and product purity [1]. However, membranes and diaphragms remain a key major challenge [3]. Practical polymers must combine high OH^- conductivity with good dimensional and mechanical stability across operating conditions, while resisting chemical degradation under strong alkaline and oxidative environments [4]. Low permeability and suppressed H_2/O_2 crossover are also essential for safety and durability. Current strategies focus on polymer blending, controlled crosslinking, incorporation of inorganic fillers, and more stable cationic chemistries [5]. Bio-derived polymers such as cellulose or chitosan are increasingly explored to improve sustainability while maintaining tunable ion transport, hydration control, and mechanical reinforcement. Progress in membrane materials, together with compatible electrodes

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and transport layers, is crucial for durable, high-current-density alkaline electrolyzer stacks and wider deployment of affordable green hydrogen [5].

This work reports the development of hybrid semi-interpenetrating xTEOS–PVA:xPVP ion-solvating membranes via acid-catalyzed sol–gel processing, solution casting, and KOH activation, and we systematically correlate chemistry, morphology, hydration, conductivity, and oxidative stability. The central hypothesis is that TEOS-derived inorganic crosslinking, combined with PVA/PVP entanglement, can generate well-solvated OH^- transport pathways while suppressing excessive swelling and improving oxidative durability. The main outcome is the identification of an optimal intermediate composition that simultaneously delivers high OH^- conductivity in 1 M KOH and enhanced oxidative stability compared with polymer-only controls.

Materials and Methods

Silica sols were synthesized via a two-step sol–gel procedure. The precursor tetraethyl orthosilicate (TEOS) (≥99.0%, Mw = 208.33 g·mol^{-1}) was dissolved in EtOH/H_2O with ethyl alcohol (≥99.5%)/ D.W with a pH of 5 and a conductivity of 14.79 µS cm^{-1} and stirred for 1 h with 1:8:4 molar ratio (TEOS:EtOH:H_2O); 0.1 M of hydrochloric acid (HCl) (37%) was added dropwise to catalyze hydrolysis [6], and the mixture was stirred at room temperature for 6 h until gelation. The gel was dried at 80 °C for 12 h to give a xerogel, which was ground to obtain silica hydrated powder. We dissolved poly(vinyl alcohol) (PVA) (average Mw 130,000, 99+% hydrolyzed) (4 g) in distilled water (100 mL) at 90 °C under vigorous stirring until the solution turned clear. A different amount of hydrolysis of TEOS (0.5, 1, 1.5, 2 g) and concentrated 1 M HCl (1 mL) were then added to trigger the sol–gel reaction. After stirring at room temperature for 2 h, we introduced an aqueous solution of PVP prepared separately by dissolving at 60 °C (2, 1.5, 1, 0.5g) of poly(vinylpyrrolidone) (PVP) (average Mw = 40 000 g·mol^{-1}), at the target TEOS-PVA:PVP ratio. The homogeneous solution was cast onto Petri dishes and left to dry under ambient conditions for 24 h. The dried films were gently peeled from the substrate, soaked in 3 M potassium hydroxide (KOH) (≥99.0%) at 60 °C for 3 h to convert them to the Ion-Solvating membrane, rinsed thoroughly with distilled water, and air-dried before characterization.

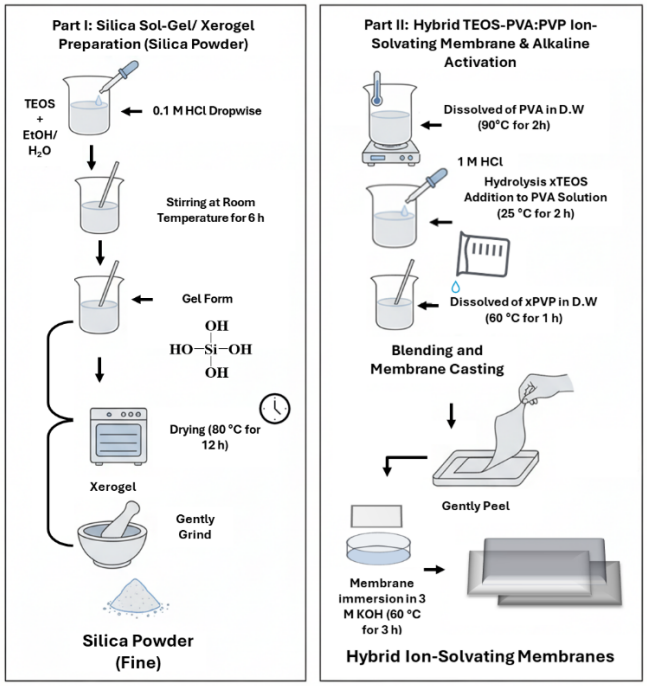


Fig. 1 *The fabrication process of hybrid TEOS-PVA:PVP ion-solvating membranes.*

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Characterization Techniques

FTIR (Fourier Transforms Infrared Spectroscopy). The reaction between PVA and TEOS blending with PVP membrane was confirmed using FTIR spectrometer (FTIR, Perkin-Elmer Spectrum 2000, Waltham, Massachusetts, United States) equipped with an ATR accessory was used. The tests were carried out with a spectral resolution of 0.5 cm^{-1}, 32 scans per spectrum and in the range 600-4000 cm^{-1}.

Morphology. The surface morphology of the hybrid ion-solvating membranes were imaged using scanning electron microscopy (SEM, ZEISS EVO 10, GmbH, Jena, Germany) operated at an accelerating voltage of 10 kV. Elemental composition analysis was performed using an energy-dispersive X-ray (EDX) analyzer. The membrane samples were vacuum dried for 20 minutes to prevent charging during imaging and subsequently coated with a gold (Au) layer via sputtering for 600 seconds.

Water Uptake and swelling ratio. For water uptake (WU) and swelling ratio (SR), membranes were immersed in deionized water for 24 hours to achieve full hydration. Before immersion, the mass and length of the dried membranes were recorded. After 24 hours, the hydrated membranes were gently wiped with tissue paper to remove surface water, and their mass and length were quickly measured [7,8]. Each test was performed five times, and the average values were reported. The WU and SR were calculated from the equations (1) and (2):

$$\mathbf{WU}(\%) = \frac{\mathbf{W_w - W_d}}{\mathbf{W_d}} \times \mathbf{100} \quad \textbf{(1)}$$

$$\mathbf{SR}(\%) = \frac{\mathbf{L_w - L_d}}{\mathbf{L_d}} \times \mathbf{100} \quad \textbf{(2)}$$

Hydroxide ion conductivity. The OH^- ionic conductivity of the membranes formed was assessed through AC impedance measurements utilizing an electrochemical impedance analyzer (Biologic SP 300). The AC frequency range spanned from 100 kHz to 100 Hz with a voltage amplitude of 10 mV. Fully hydrated membranes were equipped with two Pt counter-electrode wire (H-Cell 2x15 mL). The membrane remained in contact with 1 M of potassium hydroxide during the entire measurement process in two different temperatures, 25 °C, and 80 °C [8]. Ionic conductivity (mS/cm) was computed using the equation (3):

$$\boldsymbol{\sigma} = \frac{\mathbf{T}}{\mathbf{R \times A}} \quad \textbf{(3)}$$

Where, T is the thickness of membranes (cm), R is the bulk – without membrane resistance (Ω), and A is the surface area of membranes (cm^2) [9].

Oxidative stability. The oxidative stability of the prepared membranes was assessed by immersing them in Fenton's reagent (a solution of 3% H_2O_2 with 3 ppm $FeSO_4$) at 80 °C for 1 hour. The oxidative stability was then quantified by calculating the percentage of weight loss [10,11]. The O.S is calculated using the equation (4):

$$\mathbf{O.S}(\%) = \mathbf{100} - \left(\frac{\mathbf{W_b - W_a}}{\mathbf{W_b}} \times \mathbf{100}\right) \quad \textbf{(4)}$$

Where W_b is weight before loss, and W_a is the weight after immersing the membranes in solution.

Results and discussion

Pereparation of TEOS-PVA:PVP Hybrid Ion-Solvation Membrane. The TEOS–PVA:PVP hybrid ion-solvating membrane was prepared by combining PVA, PVP, and TEOS, followed by alkaline doping to improve OH^- transport and durability (**Fig. 2**). First, TEOS was hydrolyzed at room temperature in the presence of HCl to form a silica sol [12]. Under acidic conditions, hydrolysis dominates over condensation, producing silanol-rich siloxane oligomers [6]. Next, the silica phase was dispersed into an aqueous PVA solution and cast into films. During drying, dehydration-driven condensation formed Si–O–Si bonds within the inorganic phase and created

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interfacial interactions with PVA [6]. Condensation between silanol groups and PVA hydroxyls can also generate Si–O–C linkages (Si–OH + HO–PVA → Si–O–PVA + H_2O), strengthening the hybrid network. Although PVP does not readily form covalent bonds with silanols, it stabilizes silica dispersion through hydrogen bonding and chain entanglement, limiting aggregation and promoting a uniform microstructure, which supports higher hydration and ionic conductivity [13].

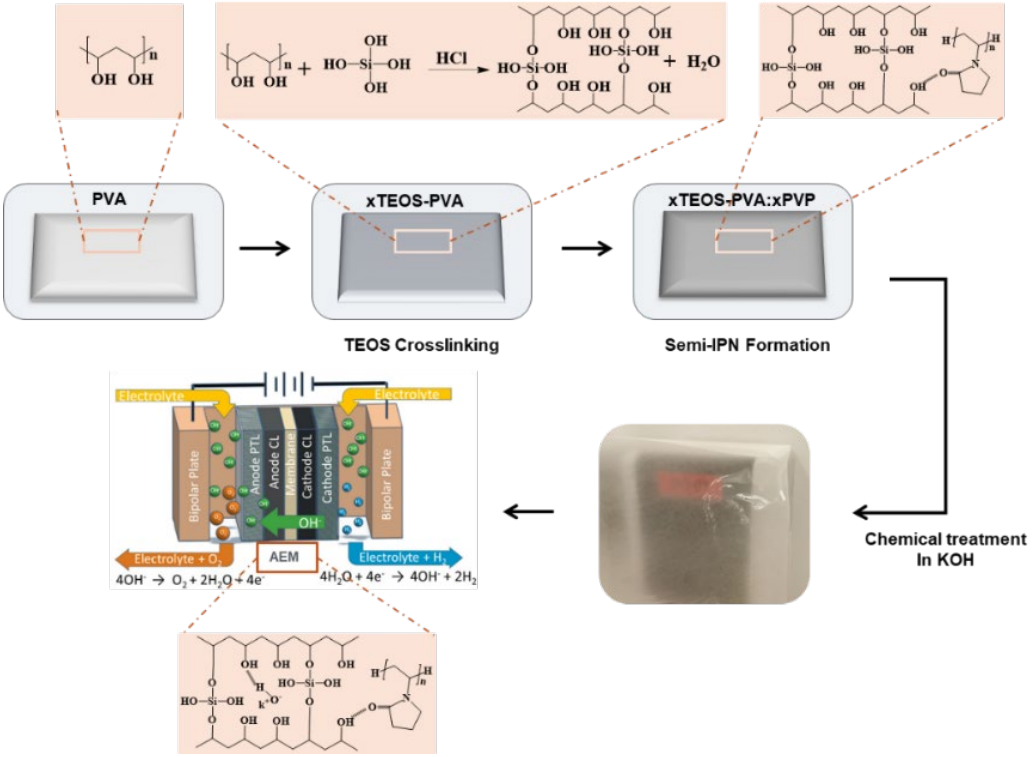


Fig. 2 *The fabrication process and Mechanism of hybrid TEOS-PVA:PVP ion-solvating membranes.*

Chemical Structural Analysis. FTIR spectra confirm the structure of PVA, PVA:PVP, and xTEOS–PVA:xPVP membranes (Fig. 3). Neat PVA shows a broad O–H band (≈3200–3570 cm^{-1}), C–H stretching (≈3000–2800 cm^{-1}), and strong C–O vibrations (≈1140–1080 cm^{-1}) [14]. Adding PVP introduces the lactam C=O band (≈1680–1630 cm^{-1}) and slightly shifts and broadens the O–H band, indicating stronger PVA–PVP hydrogen bonding. With TEOS (0.5T–2T), the growth of bands at ≈1100–1040, ≈950, and ≈800–750 cm^{-1} is consistent with Si–O–Si and Si–O–C formation during sol–gel condensation, while the further red-shift of O–H suggests increased interaction and partial consumption of PVA hydroxyls [15]. Overall, the spectra support formation of a hybrid PVA–SiO_x network where PVP mainly contributes through hydrogen bonding and TEOS provides inorganic crosslinking.

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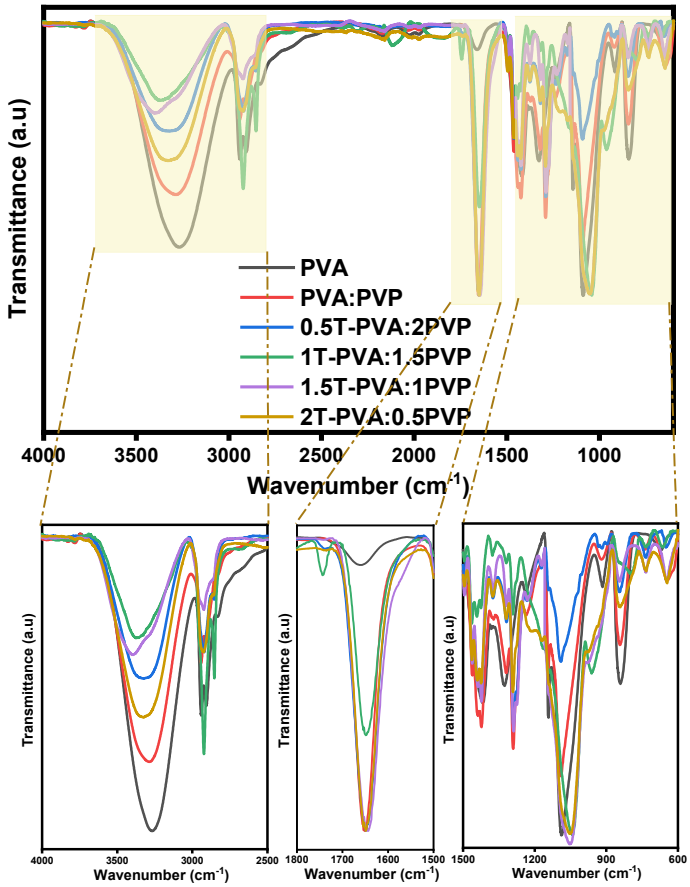


Fig. 3 *FTIR Spectrum of the fabricated Ion-Solvating Membranes*

Morphology. SEM observations support the FTIR results and show how TEOS and PVP control membrane morphology (**Fig. 4**). Neat PVA is compact, and the PVA:PVP blend remains smooth due to strong PVA–PVP hydrogen bonding. With TEOS addition, the surface evolves from mostly dense (0.5T–2PVP) to a fine, homogeneous nodular texture (1T–1.5PVP), then to a more pronounced bicontinuous or sponge like structure at intermediate composition (1.5T–1PVP), indicating stronger silica condensation and microphase separation. At the highest TEOS and lowest PVP (2T–0.5PVP), the surface becomes re-densified and fused, consistent with over-condensation and silica aggregation when PVP stabilization is limited. Overall, high PVP maintains dense films, intermediate PVP promotes a well-distributed hybrid network, and low PVP at high TEOS leads to densification, in agreement with the FTIR siloxane growth and reduced free –OH.

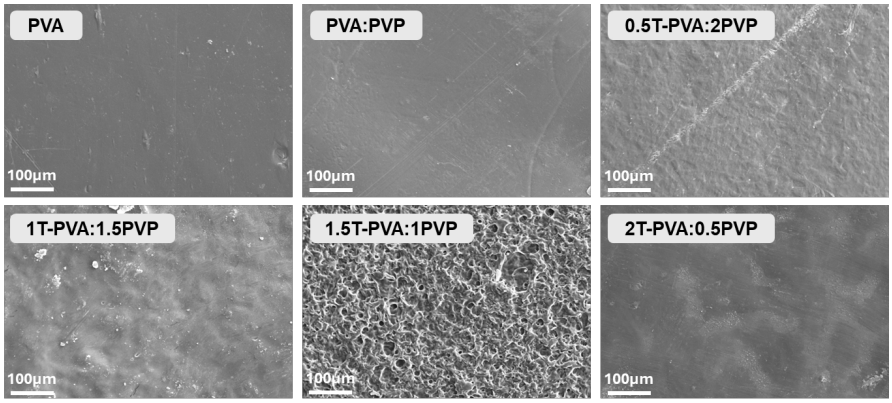


Fig. 4 *Surface Morphology of Ion-Solvating Membranes*

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Water Uptake and swelling ratio. Neat PVA (**Fig. 5a**) shows the highest water uptake (~374.4%) and moderate swelling (~16.2%) due to its abundant –OH groups. Adding PVP reduces both uptake (~286.3%) and swelling (~11.4%), consistent with stronger PVA–PVP hydrogen bonding and a denser matrix. At low TEOS with high PVP (0.5T–PVA:2PVP), uptake remains high (~314.3%) and swelling reaches a maximum (~33.3%), likely due to additional hydrophilic silanol groups. Increasing TEOS to 1T–PVA:1.5PVP decreases both values, indicating the onset of inorganic crosslinking. A strong reduction is observed at 1.5T–PVA:1PVP (uptake ~77.6%; swelling ~3.3%), reflecting extensive Si–O–Si/Si–O–C network formation that restricts hydration and dimensional change. At 2T–PVA:0.5PVP, uptake partially increases (~97.0%) while swelling remains limited (~13.3%), consistent with a dense hybrid network that can bind water but suppresses expansion. Overall, the hydration and swelling behavior follows the FTIR/SEM trends: PVP reduces free –OH, low TEOS increases hydrophilicity, and higher TEOS crosslinking limits water uptake and swelling.

Hydroxide ion conductivity. At 25 and 80 °C in 1 M KOH, both PVA and PVA:PVP show low hydroxide conductivity (**Fig. 5b**): 9 and 42.85 mS cm^{-1} for PVA, and 8.78 and 37.5 mS cm^{-1} for PVA:PVP, respectively. Adding a small TEOS amount at high PVP (0.5T–PVA:2PVP) strongly increases conductivity to 90 mS cm^{-1} (25 °C) and 150 mS cm^{-1} (80 °C). At 1T–PVA:1.5PVP, conductivity decreases but remains high (60 and 100 mS cm^{-1}), consistent with sufficient hydration and controlled swelling that maintain continuous solvated pathways. Further increasing TEOS while reducing PVP (1.5T–PVA:1PVP) sharply lowers conductivity (5.62 and 13.63 mS cm^{-1}), in line with reduced water uptake and a more rigid, highly crosslinked matrix. At 2T–PVA:0.5PVP, conductivity slightly recovers (8.18 and 23.07 mS cm^{-1}) but remains limited, indicating that restricted hydration and polymer mobility govern OH^- transport at high TEOS loading. The membranes are benchmarked against representative PVA-based hybrid membranes and other alkaline membrane systems reported in the literature. Reported performance depends strongly on testing conditions (electrolyte concentration, temperature, cell setup, pre-treatment, thickness, and measurement method). For this reason, the comparison focuses mainly on studies evaluated under similar conditions (e.g., conductivity measured in KOH at comparable concentration and temperature). Table 1 summarizes the key parameters, including composition, conductivity, water uptake, and stability. The optimized semi-interpenetrating TEOS–PVA:PVP membrane combines high OH^- conductivity in alkaline media with improved oxidative stability and controlled hydration, supporting its competitiveness among PVA-based hybrid ion-transport membranes.

Oxidative stability. Neat PVA shows low oxidative stability, and only a limited improvement is observed after blending with PVP. In contrast, TEOS incorporation significantly increases oxidative resistance (**Fig. 5c**). The 0.5T–PVA:2PVP membrane shows moderate retention (~62.7%), consistent with a mostly organic matrix. The highest stability is obtained for 1T–PVA:1.5PVP (~90%), indicating that an adequately condensed hybrid network effectively limits degradation and mass loss. At higher TEOS loadings, retention remains high but slightly lower (1.5T–PVA:1PVP ~81%; 2T–PVA:0.5PVP ~83%), likely due to increased densification and microstructural heterogeneity. Overall, the results indicate that forming Si–O–Si/Si–O–C linkages improves oxidative durability, with the best performance at an intermediate TEOS/PVP ratio.

Table 1 *Comparison of water uptake/swelling ratio, hydroxide conductivity and oxidative stability between the 0.5T-PVA:2PVP, 1T–PVA:1.5PVP membranes and commercial AEMs at 80 °C.*

Membrane	Water Uptake (%)	Swelling Ratio (%)	σ at 80 °C (mS cm⁻¹)	Oxidative Stability (%)	Ref
0.5T–PVA:2PVP	314.28	33.33	150	62.66	This work
1T–PVA:1.5PVP	292.85	16.66	100	90	This work
Sustainion® X37-50	80	15.1	140	N/A	[16]
Tokuyama A201	44 (80 °C)	12 (80 °C)	60–90	N/A	[16]

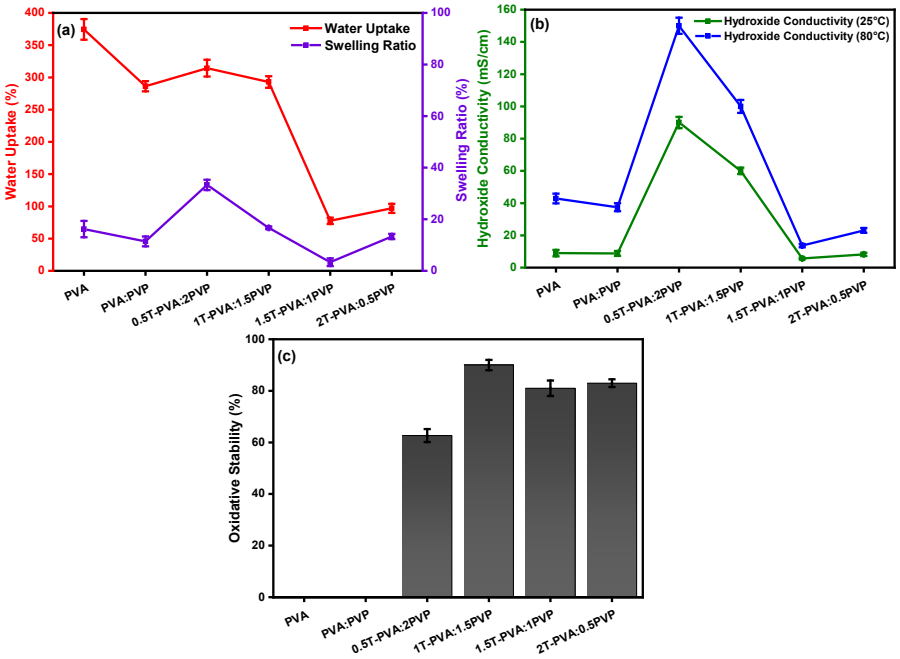


Fig. 5 (a) *Water uptake and Swelling Ratio,* ***(b)*** *Ionic Conductivity at 25-80 °C,* ***(c)*** *Oxidative Stability of Ion-Solvating Membranes*

Conclusion

Hybrid semi-interpenetrating xTEOS–PVA:xPVP ion-solvating membranes were fabricated by a simple sol–gel/casting method followed by KOH activation. TEOS forms Si–O–Si and Si–O–C crosslinks, which tune morphology and hydration. Increasing TEOS reduces water uptake and swelling, while hydroxide conductivity reaches its optimum at 1T–PVA:1.5PVP (~60 mS cm^{-1} at 25 °C; ~100 mS·cm^{-1} at 80 °C) with high oxidative stability (~90% mass retention). Overall, this intermediate composition offers high OH^- transport with controlled swelling and improved durability, making it promising for alkaline membrane electrolyzers. This work will focus on extended durability testing under realistic AEMWE operation, gas crossover, permeability measurements, and mechanical evaluation after alkaline aging, as well as assessing scalability through controlled thickness casting and reproducibility.

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