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Evaluation of sulfonated chitosan-g-sulfonated polyvinyl alcohol/polyethylene oxide/sulfated zirconia composite polyelectrolyte membranes for direct borohydride fuel cells: Solution casting against the electrospun membrane fabrication technique

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To improve the mechanical properties of proton exchange membranes, consequently improving the performance of direct borohydride fuel cells, the present study prepared sulfonated chitosan-g-sulfonated polyvinyl alcohol/polyethylene oxide doped with sulfated zirconia composite (SCS-g-SPVA/PEO/SZrO₂) polyelectrolyte membranes. Two fabrication techniques were followed, solution casting and electrospinning, to have the membranes in film and fiber forms and study the effect of the different forms on the membrane's physicochemical properties. For the casting technique, different concentrations of SZrO₂ (1–3 wt%) were used, while the optimum concentration of SZrO₂ (3 wt%) was used in the electrospun one (SCS-g-SPVA/PEO/SZrO₂-CF). SCS-g-SPVA/PEO/SZrO₂-C membranes were prepared in a single step. The grafting and the crosslinking were carried out using glutaraldehyde and sulfosuccinic acid as sulfonating agents for chitosan and PVA and coupling agents simultaneously using click chemistry. On the other hand, SCS-g-SPVA/PEO/SZrO₂-CF membranes were prepared in two steps. They were fabricated with electrospinning and then dipped into the

coupling and crosslinking solutions. The casting membranes' physicochemical properties were improved by increasing the SZrO_2 content. The experimental results further show that the fabrication procedure significantly influences the physicochemical properties of the membranes. For instance, the composite fiber membrane demonstrated higher selectivity and higher ion exchange capacity (IEC) than the casting membrane. Furthermore, by using the response surface methodology model, the effects of ion exchange capacity, water uptake, and oxidative stability were optimized as three independent variables that affected the ionic conductivity of SCS-g-SPVA/PEO/ SZrO_2 -3C. The optimized ionic conductivity of the SCS-g-SPVA/PEO/ SZrO_2 -3C membrane was 13.6 mS cm^{-1} , achieved at the maximum point of the polynomial model, with an IEC of 0.74 meq g^{-1} , $\sim 92\%$ water uptake, and about 93% oxidative stability.

KEYWORDS

proton exchange membranes, polyvinyl alcohol, polyethylene oxide, chitosan, electrospun, direct borohydride fuel cell

Introduction

A fuel cell is considered one of the most favorable energy resources (Gouda et al., 2020a; Mohy Eldin et al., 2020; Gouda et al., 2021a). It collects the merits of batteries and heat engines and simultaneously avoids their disadvantages. Zero pollution and high efficiency became achievable by a fuel cell, where chemical energy is directly converted to electricity (Gouda et al., 2020b; Gouda et al., 2021b; Gouda et al., 2021c). A fuel cell can provide uninterrupted power as long as reactants are fed to the cell, with both fuel and oxidant being stored externally.

A direct borohydride fuel cell (DBFC) is an electrochemical device that generates electrical energy by the electroreduction of hydrogen peroxide (as the oxidant) at the cathode and the electrooxidation of borohydride (as the fuel) at the anode. Compared with direct alcohol fuel cells or conventional hydrogen-fed polymer electrolyte fuel cells, DBFCs have suitable energy and thermodynamic characteristics (Gouda et al., 2019a; Gouda et al., 2020c; Gouda et al., 2020d).

Proton-exchange membranes (PEM), from which Nafion[®] is the current benchmark membrane, are an essential component of fuel cells. They work as electron insulators and prevent fuel crossover between electrodes (Gouda et al., 2019b). However, fuel permeability is still an important issue due to the osmotic drag and diffusion, which lower the power density output. Several studies have focused on the transfer of ions or protons *via* polymeric membranes and new ideas for enhancing its qualities. Still, the high cost of the Nafion[®] and its fuel permeability has not been solved yet. Therefore, to increase the possibility of DBFCs commercialization, it would be necessary to replace Nafion[®] membranes with alternative cheap and green membranes. For this purpose, poly (vinyl alcohol) (PVA) membranes could be an excellent choice.

PVA is a synthetic polymer, cheap, chemically stable, and nontoxic (Gouda et al., 2021d; Gouda et al., 2021e; Gouda et al.,

2021f; Gouda et al., 2021g). In acidic media, the hydroxyl groups of PVA and chitosan (CS) bond with aldehyde groups of glutaraldehyde to form hemiacetal or acetal linkages (Gouda et al., 2021f). Moreover, PVA and CS functional groups (-OH) react with carboxylic groups of sulfosuccinic acid by esterification reaction to crosslink and sulfonate PVA and CS simultaneously. Resultant crosslinked sulfonated PVA (SPVA) and sulfonated CS (SCS) membranes are water-insoluble and suitable for proton conduction and electronic insulation in fuel cells. Blending and crosslinking a synthetic polymer such as PVA with a natural polymer such as CS has a positive effect on enhancing ionic conductivity (Yang et al., 2018). CS is a cationic polysaccharide, nontoxic, inexpensive, natural, and biodegradable polymer (Yang et al., 2004; Divya and Jisha, 2018). It is insoluble in most organic solvents and water. However, it is soluble in some weak dilute organic acids, like acetic acid.

Polyethylene oxide (PEO) is broadly used as a film-forming synthetic polymer with flexibility, good tensile strength, and high PVA compatibility. It can form a hydrogen bond network with the CS and PVA matrix (Rochliadi et al., 2015; Deshmukh et al., 2016). When ceramic inorganic acid like sulfated zirconia (SZrO_2) is calcined at 300°C , it enhances ionic conductivity (14.5 mS cm^{-1}), with an ion-exchange capacity of 0.54 meq g^{-1} and higher water uptake due to sulfate ions, the SZrO_2 addition increases the sulfate ions content inside the polymeric membrane (Saccà et al., 2006; Navarra et al., 2008; Tominaka et al., 2010; Giffin et al., 2012). Also, the addition of SZrO_2 to the membrane leads to additional ions within the PVA matrix (Gouda et al., 2021a). Gouda et al. (2021f) reported that a PVA blend membrane containing nano SZrO_2 exhibited lower fuel permeability, lower swelling, and improved mechanical properties.

Nanofibers with average diameters $<1,000 \text{ nm}$ are nanomaterials used in the industrial and academic research (Yang et al., 2018). Electrospinning (Ballengee and Pintauro,

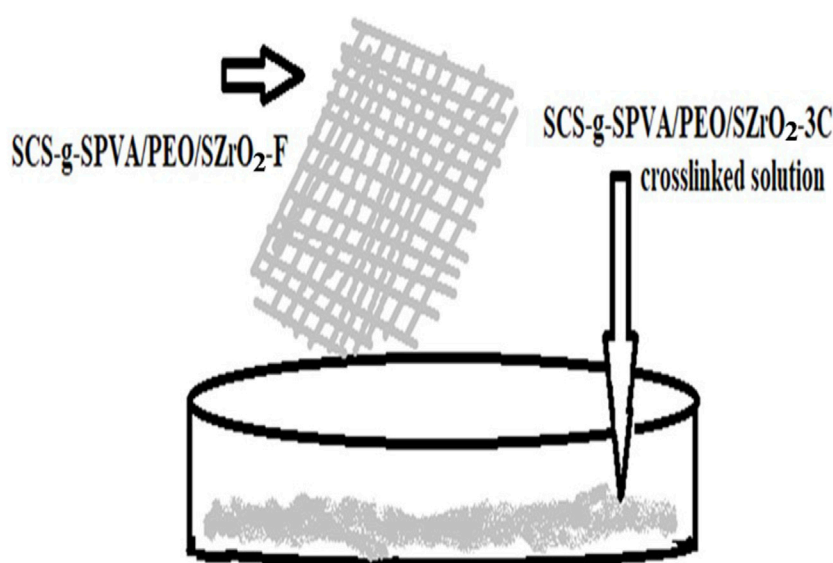


FIGURE 1
Preparation of composite fiber membrane.

TABLE 1 Level of various independent variables at coded values of response surface methodology experimental design.

Symbol	Independent variables	Coded levels		
		-1	0	1
A	IEC/meq g ⁻¹	0.4	0.6	0.8
B	water uptake/%	10	60	110
C	oxidative stability/RW%	80	90	100

2011; Ballengee et al., 2013; Ballengee and Pintauro, 2013; Zizhou et al., 2021) and bubble electrospinning (Liu et al., 2021; He et al., 2022; Qian and He, 2022) are practical and cost-effective approaches for preparing different types of nanofibers. The conductivity improvement in electrospun nanofiber membranes (Box and Behnken, 1960; Dong et al., 2010; Lin et al., 2010; Yao et al., 2011a; Yao et al., 2011b; Li et al., 2014) has been reported. Compared to conventional polymeric membranes, nanofiber membranes appeared to have distinct anion and proton conductive properties. PVA/CS membranes fabricated by casting were compared with those fabricated by electrospinning techniques, and the performance of the two membranes was very close (Yang et al., 2018).

To contribute to the dissemination and future commercialization of borohydride fuel cells, we are developing low-cost and green-prepared membranes with better oxidative stability, tensile strength, and lower borohydride permeability than Nafion. Herein two types of SCS-g-SPVA/PEO/SZrO₂ proton exchange membranes have been fabricated. The first one, SCS-

g-SPVA/PEO/SZrO₂-C, was prepared by casting method, by crosslinking with sulfosuccinic acid and glutaraldehyde, and then doped with different concentrations of SZrO₂ (1-3 wt%). The second was fabricated using the electrospinning technique, leading to composite electrospun nanofiber membranes, SCS-g-SPVA/PEO/SZrO₂-CF. The characterization of these two membranes was studied with TGA, DSC, and FTIR. Also, water uptake, fuel permeability, ionic conductivity, and selectivity were measured. The aim of blending the three green polymers is to create a network of hydrogen bonds that promotes proton transport across the membrane. Additionally, combining the three polymers leads to a functionalized nanomaterial that enhances the membrane's mechanical properties.

Materials and methods

Preparation of sulfated zirconia and SCS-g-SPVA/PEO/SZrO₂-C casting membranes

The fabrication steps of SZrO₂ were detailed in our previous studies (Gouda et al., 2021a; Gouda et al., 2021f). The membranes preparation was as follows: 10 wt% PVA solution was prepared by dissolving PVA (99% hydrolysis, medium MW, Sigma-Aldrich, United States) in water at 90°C for 2 h with vigorous stirring to obtain a clear solution. The chitosan clear solution was obtained by stirring 2 wt% CS (Sigma-Aldrich, United States) in 50 ml water with adding 1 ml acetic acid solution. The PEO solution was prepared by dissolving 2 wt% of PEO (average MW:

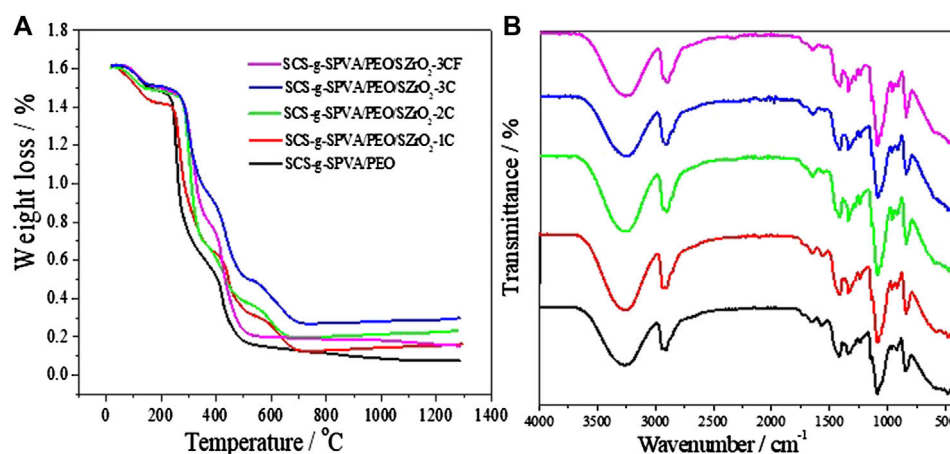


FIGURE 2
(A) TGA curves and (B) FTIR spectra of the nanocomposite membranes.

TABLE 2 The melting point of membranes formed from DSC.

Sample	Melting point/°C
SCS-g-SPVA/PEO	225 ± 3
SCS-g-SPVA/PEO/SZrO ₂ -1C	219 ± 2
SCS-g-SPVA/PEO/SZrO ₂ -2C	216 ± 2
SCS-g-SPVA/PEO/SZrO ₂ -3C	212 ± 2
SCS-g-SPVA/PEO/SZrO ₂ -3CF	210 ± 2

900,000 g mol⁻¹, Acros Organics, United States) in 50 ml of water: ethanol (50:50 vol%) mixture at room temperature. CS and PEO were then added to the PVA solution to form a blend of the PVA/CS/PEO solution by stirring for 2 h. The wt% in the PVA:CS:PEO blend is ca. 70:15:15.

For casting membrane preparation, the polymeric blend was crosslinked and sulfonated by adding 10 ml of sulfosuccinic acid (99.9 wt% in H₂O, Sigma-Aldrich, United States) and 0.5 ml of glutaraldehyde (GA) (50 wt% in H₂O, Alfa Aesar, United States) in 10 ml of acetone and thorough stirring for 4 h at 40°C, followed by adding different concentrations of SZrO₂ (1–3 wt% with respect to PVA) in the form of a suspension in few drops of water. The membranes formed were named SCS-g-SPVA/PEO/SZrO₂-1C, SCS-g-SPVA/PEO/SZrO₂-2C, and SCS-g-SPVA/PEO/SZrO₂-3C, relative to the SZrO₂ wt%. The mixture solution was poured into Petri dishes and dried overnight at 70°C in a vacuum oven.

Preparation of SCS-g-SPVA/PEO/SZrO₂-CF composite nanofiber membranes

The preparation of SCS-g-SPVA/PEO/SZrO₂-CF composite nanofiber membranes involved the following steps: 1) the SCS-g-

SPVA/PEO/SZrO₂-F electrospun nanofiber was first prepared with 3 wt% of SZrO₂, then 2) SCS-g-SPVA/PEO/SZrO₂-F was crosslinked by the same crosslinkers of glutaraldehyde and sulfosuccinic acid, finally 3) SCS-g-SPVA/PEO/SZrO₂-F was dipped into the crosslinked SCS-g-SPVA/PEO/SZrO₂-3 solution.

For comparison purposes, the SCS-g-SPVA/PEO/SZrO₂-3C membrane was fabricated in nanofiber shape because this casting membrane realized the best physicochemical properties in terms of fuel permeability, water uptake, and ionic conductivity. The SCS-g-SPVA/PEO/SZrO₂-3C solution (without crosslinkers) was injected in a 10 ml syringe, and the voltage applied was 20 kV. The distance between the syringe needle and the fixed collector was 15 cm. To fill the macro-voids between fibers and crosslink the nanofiber membrane (to enhance mechanical strength), the prepared SCS-g-SPVA/PEO/SZrO₂-3F nanofiber membrane was dipped in the crosslinked SCS-g-SPVA/PEO/SZrO₂-3C solution for a few minutes, then dried overnight at 70°C in a vacuum oven to obtain SPVA/PEO/SZrO₂-3CF, as shown in Figure 1.

Membrane characterization

The prepared membranes' thermal properties and functional groups were evaluated with TGA (Shimadzu TGA-50, Japan) and FTIR (Shimadzu FTIR-8400 S- Japan). The morphologies of electrospun SCS-g-SPVA/PEO/SZrO₂-3F membrane and SCS-g-SPVA/PEO/SZrO₂-3C were observed with SEM (JEOL Jsm 6360LA-Japan). ImageJ software evaluated the diameter distribution of the SCS-g-SPVA/PEO/SZrO₂-3F electrospun nanofibers. The physicochemical and electrochemical tests measured tensile strength, water uptake, ion exchange capacity (IEC), swelling ratio, borohydride permeability, oxidative

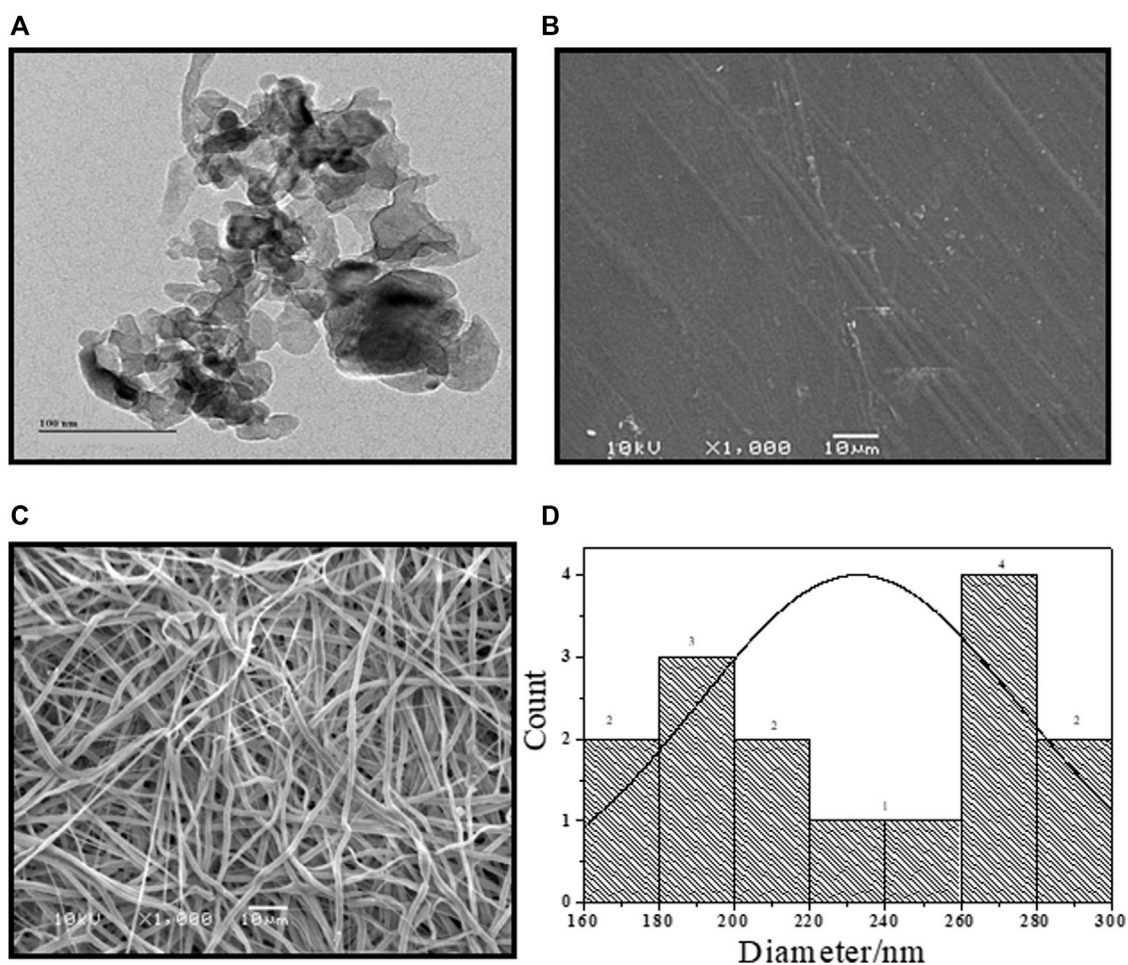


FIGURE 3

TEM images of (A) SZrO₂, the SEM image of (B) SCS-g-SPVA/PEO/SZrO₂-3C and (C) SCS-g-SPVA/PEO/SZrO₂-3F, and (D) average diameter distribution of SPVA/PEO/SZrO₂-3F.

stability, ionic conductivity, and selectivity. The procedures and devices are detailed in our previous study (Gouda et al., 2019b; Gouda et al., 2020d) and in the [Supplementary Material](#).

Optimizing membrane properties and their effect on ionic conductivity

Design-Expert, 13.0.9.0 program from STAT-EASE, INC was used for the experimental design, model construction, and data analysis. The Box Behnken design (Elessawy et al., 2020) with three variables were used to determine the response pattern and create a model. Because distinct variables are typically expressed in different units and have varying limitations, the significance of their impacts on response can only be compared once they have been coded. In this study, the effects of three independent variables, A (ion exchange capacity), B (water uptake), and C

(oxidative stability), at three levels were chosen as three independent variables that affected the ionic conductivity of SCS-g-SPVA/PEO/SZrO₂-3C (Y). The range and values of these three independent variables, presented in [Table 1](#), were based on data from preliminary experiments. Furthermore, the developed polynomial models were statistically validated using analysis of variance (ANOVA), with the F-test used to check their statistical significance. The coefficient of determination R^2 was used to check their fitting quality (Ming Yang and Chih Chiu, 2012).

Results and discussion

Characterization of different membranes

As shown in [Figure 2A](#), three stages of weight loss appeared for PVA-based composites with TGA (Gouda et al., 2021f). The

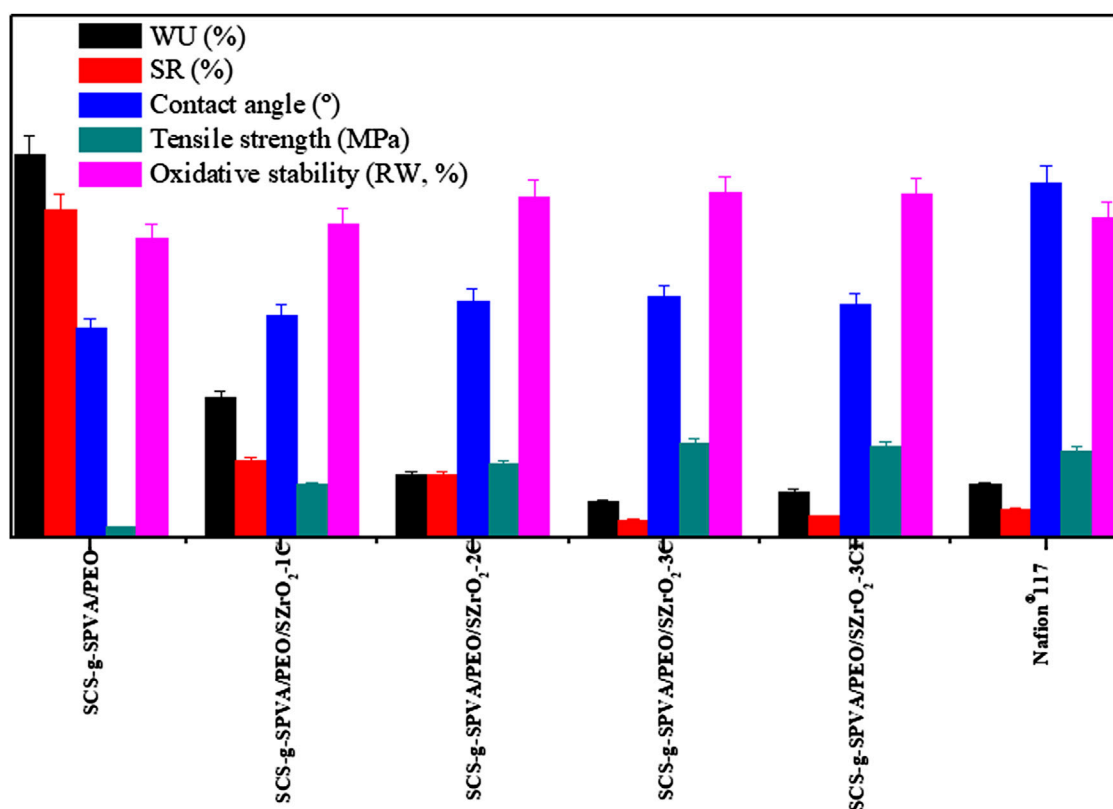


FIGURE 4
Physicochemical properties of the prepared membranes and Nafion®117.

first is due to moisture evaporation around (50–150°C), while the second concerns the functional groups' degradation (ca. 150–250°C), and the last stage is due to polymers backbone degradation (250–450°C). It can also be noted that the thermal degradation temperature shifted to higher temperatures as the SZrO₂ content increased. That means the thermal stability is improved in SPVA/PEO/SZrO₂-3C and SPVA/PEO/SZrO₂-3CF membranes due to the presence of sulfated zirconia with optimum content, which supports the membranes by increasing the hydrogen bond network. As illustrated in Table 2, the melting point of the membranes decreased with the increasing SZrO₂ content. The decrease in the melting point of membranes is due to hydrogen bonds formed between sulfated zirconia and polymers' functional groups, which reduces the crystallinity of the membranes (Gouda et al., 2021f; Gouda et al., 2021g). All functional groups in the membrane matrix can be confirmed from the FTIR spectrum, as shown in Figure 2B. The broad peaks at 3,250–3,500 cm⁻¹ refer to -OH groups of PVA and CS, and those at about 1,415 and 1,085 cm⁻¹ are attributed to -C-O groups (Yang and Su, 2011). The peak at 1,580 cm⁻¹ is due to the NH₂ group in pure chitosan (Osman and Arof, 2003; Mauricio-Sánchez et al., 2018). The peaks between 900 and

1,200 cm⁻¹ refer to the sulfate group in the doping agent and crosslinker, while the Zr-O bond was found at 470 cm⁻¹.

TEM micrographs of SZrO₂ demonstrate that the sulfated zirconia was fabricated in an irregular shape with a nanosize scale (Figure 3A). The surface of the casting membrane, SCS-g-SPVA/PEO/SZrO₂-3C, appeared without agglomeration or pores (Figure 3B). In contrast, SCS-g-SPVA/PEO/SZrO₂-3F membranes appeared in the fiber shape (Figure 3C). The average diameter distribution of SPVA/PEO/SZrO₂-3F nanofibers is presented in Figure 3D, with the diameters ranging between 20 and 280 nm.

Physicochemical and electrochemical properties of membranes

It can be noted from Figure 4 and Supplementary Table S6 in Supplementary Materials that all the fabricated membranes have hydrophilic nature because all contact angles were <90° (Gouda et al., 2020d). In addition, the thickness of membranes increased with the doping agent content. Also, the water uptake and the swelling ratio dramatically decreased with increasing SZrO₂ because it filled all membrane voids and converted the

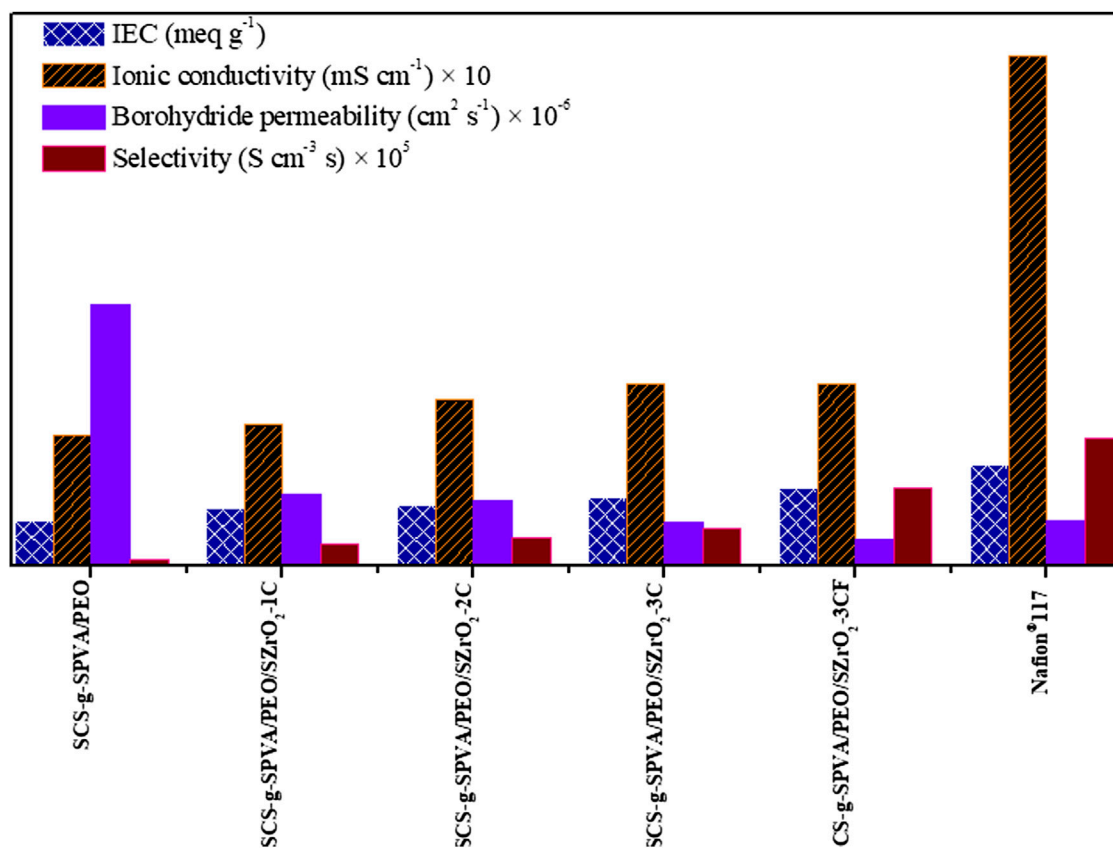


FIGURE 5

Ion exchange capacity, ionic conductivity, borohydride permeability, and selectivity of the prepared membranes and Nafion®117.

TABLE 3 The Box-Behnken design matrix and results for the three variables that influence the ionic conductivity of the SCS-g-SPVA/PEO/SZrO₂-3C membrane.

Trial	IEC (A; meq g ⁻¹)	Water uptake (B; %)	Oxidative stability (C; %)	Ionic conductivity (mS cm ⁻¹)	
				Measured	Curve fitted values
1	0.8	60	100	16.0	15.7
2	0.8	60	80	15.2	15.1
3	0.4	110	90	11.0	11.1
4	0.4	60	100	13.0	13.1
5	0.6	60	90	13.8	13.9
6	0.6	110	80	12.9	12.5
7	0.4	10	90	14.0	13.5
8	0.4	60	80	12.6	12.9
9	0.6	10	80	14.9	15.1
10	0.6	110	100	12.8	12.6
11	0.6	60	90	14.1	13.9
12	0.6	10	100	15.3	15.7
13	0.8	10	90	16.3	16.2
14	0.8	110	90	12.5	13.0
15	0.6	60	90	13.8	13.9
16	0.6	60	90	13.8	13.9
17	0.6	60	90	13.8	13.9

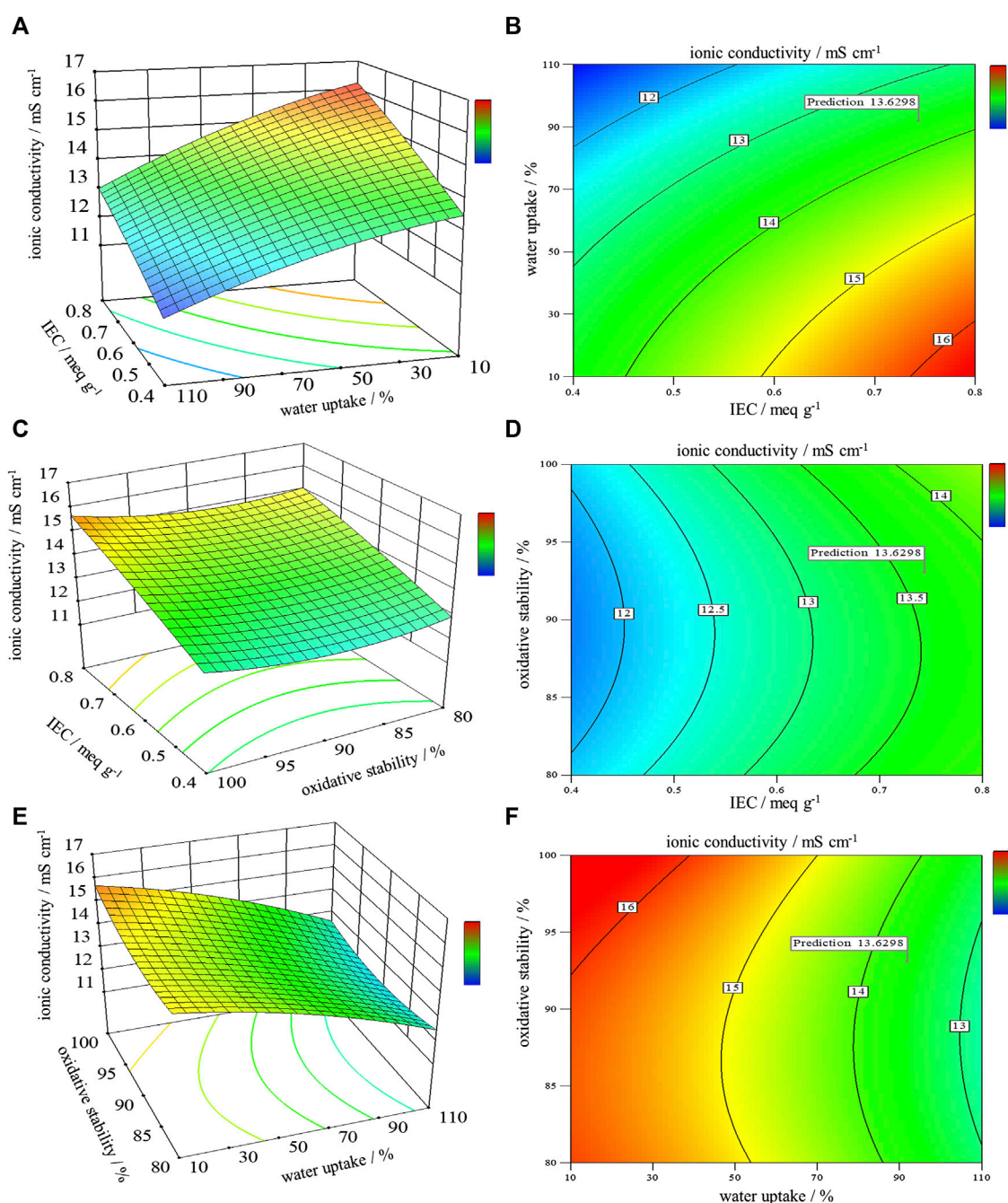


FIGURE 6

(A,C,E) 3D surface plots and (B,D,F) 2D surface plots of the interactive effects of IEC, oxidative stability, and water uptake on the ionic conductivity of the SCS-g-SPVA/PEO/SZrO₂-3C membrane.

membranes into compact and denser structures (Gouda et al., 2021f). Fenton's reagent test evaluated the oxidative stability of the membranes. The SCS-g-SPVA/PEO membrane appeared to have the lowest oxidative stability, with the addition of SZrO₂ enhancing the resistance of the membrane to radical attack. SCS-g-SPVA/PEO/SZrO₂-3C and SCS-g-SPVA/PEO/SZrO₂-3CF

membranes appeared the complete stability nearly intact (RW 99 and 98.5%), which demonstrates that SZrO₂ increases the chemical stability of the polymeric structure (Gouda et al., 2021a). The tensile strength increased with increasing SZrO₂ due to increasing the bonds in the matrix, such as the hydrogen bonds (Gouda et al., 2021a; Gouda et al., 2021f). SCS-g-SPVA/

PEO/SZrO₂-3C and SCS-g-SPVA/PEO/SZrO₂-3CF membranes presented a tensile strength of 27 and 26.5 MPa, respectively, which is higher than that of Nafion[®]117 (25 MPa).

In Figure 5 and Supplementary Table S7 of Supplementary Material, it can be noted that increasing SZrO₂ concentration as a doping agent in the membranes not only decreases the borohydride permeability but also increases the ionic conductivity and selectivity. SCS-g-SPVA/PEO/SZrO₂-3C and SCS-g-SPVA/PEO/SZrO₂-3CF achieved a BH₄⁻ permeability of 3.8×10^{-7} and 2.3×10^{-7} cm² s⁻¹, respectively, which were lower than Nafion[®]117 (4×10^{-7} cm² s⁻¹). That may owe to SZrO₂ nanoparticles acting as blocks to the migration of borohydride ions through the membrane (Shaari et al., 2018). Furthermore, when SZrO₂ is doped into the polymer matrix, hydrogen bonds are formed between the polymer chains' oxygenated and OH⁻ groups and SZrO₂. Moreover, the membrane matrix is compressed and strengthened due to the increased number of proton delivery sites provided by the hydrogen bonds, which are present in the sulfate radicals from the nanocomposite's structure. This limits excessive water absorption and swelling and improves the membrane ion-conducting properties (Shaari et al., 2018; Gouda et al., 2021f). SCS-g-SPVA/PEO/SZrO₂-3C and SCS-g-SPVA/PEO/SZrO₂-3CF attained the same ionic conductivity (16 mS cm⁻¹). On the other hand, SCS-g-SPVA/PEO/SZrO₂-3CF achieved the best selectivity (0.69×10^5 S cm⁻³ s), which means it can be a potential candidate for DBFCs. In addition, it is substantially less expensive than Nafion, which costs around 90 \$ m⁻², while SCS-g-SPVA/PEO/SZrO₂-3CF cost is about 40 \$ m⁻².

Optimizing the ionic conductivity of the SCS-g-SPVA/PEO/SZrO₂-3C membrane

In this study, we conduct an optimization step to ensure the optimum effect of the IEC, water uptake, and oxidative stability on the ionic conductivity of the SCS-g-SPVA/PEO/SZrO₂-3C membrane, which in turn increases the overall DBFC performance. To the best of our knowledge, only a few publications have addressed the optimization of PEMs in fuel cells using RSM. For instance, Shaari and Kamarudin studied the optimal content of SGO and glycerol as an additive on the selectivity of sodium alginate-based biomembrane (Shaari and Kamarudin, 2018). The actual design of this study is presented in Table 3. 3D and 2D contour plots, as shown in Figure 6, illustrate the interactive effects of the three independent variables most affecting the ionic conductivity of the SCS-g-SPVA/PEO/SZrO₂-3C membrane. The response variable was fitted with a quadratic equation that describes the process:

$$Y(\text{ionic conductivity}) = 13.86 + 1.18A - 1.41B + 0.1875C - 0.2AB + 0.1AC - 0.125BC - 0.0925A^2 - 0.3175B^2 + 0.4325C^2$$

The ANOVA analysis of variance is well-known for determining the statistical significance of the quadratic response surface model. As shown in Table 4, the quadratic model is suitable for attaining a high coefficient of determination R^2 (0.9586). The F-value of 18.03 implies that the model is significant (Shaari and Kamarudin, 2018; Elessawy et al., 2022). There is only a 0.05% chance that an F-value this large could occur due to noise. *p*-values less than 0.0500 indicate model terms are significant. There is only a 0.62% chance that a Lack of

TABLE 4 ANOVA analysis for response function Y (ionic conductivity/mS cm⁻¹).

Source	Sum of squares	df	Mean square	F-value	<i>p</i> -value
Model	28.74	9	3.19	18.03	0.0005
A-IEC	11.05	1	11.05	62.38	<0.0001
B-Water uptake	15.96	1	15.96	90.14	<0.0001
C-oxidative stability	0.28	1	0.28	1.59	0.25
AB	0.16	1	0.16	0.90	0.37
AC	0.04	1	0.04	0.23	0.65
BC	0.06	1	0.06	0.35	0.57
A ²	0.04	1	0.04	0.20	0.67
B ²	0.42	1	0.42	2.4	0.17
C ²	0.79	1	0.79	4.45	0.07
Residual	1.24	7	0.18		
Lack of Fit	1.17	3	0.39	21.62	0.006
Pure Error	0.072	4	0.018		
Cor Total	29.98	16			
Std. Dev	0.4208	R ²	0.9586		
Mean	13.87	Adjusted R ²	0.9055		
C.V.%	3.03	Predicted R ²	0.3731		
Adeq Precision	16.0347				

Fit F-value this large could occur due to noise. A deq precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 16.035 indicates an adequate signal. This model can be used to navigate the design space. The optimal levels of the three components at the maximum point of the polynomial model were 0.74 meq g⁻¹ for IEC, ~92% water uptake, and about 93% oxidative stability. This leads to about 13.6 mS cm⁻¹ for the optimized ionic conductivity of the SCS-gSPVA/PEO/SZrO₂-3C membrane, with good mechanical properties compared to Nafion[®]117.

Conclusion

This study prepared SCS-g-SPVA/PEO/SZrO₂ membranes by casting and electrospinning methods. The electrospun membrane was dipped in crosslinked polymeric casting solution to form a composite nanofiber membrane. By comparing the physicochemical properties of the two types of membranes, it was found that the BH₄⁻ permeability of the composite fiber membrane (2.3 × 10⁻⁷ cm² s⁻¹) was lower than the casting one (3.8 × 10⁻⁷ cm² s⁻¹). The ionic conductivity was the same for the two membrane types (16 mS cm⁻¹). Both the composite fiber and the casting membranes achieved lower fuel permeability, higher tensile strength, and better oxidative stability than Nafion[®]117. The composite fiber membrane demonstrated higher selectivity than the casting membrane, meaning that the fabrication method has a significant effect on the physicochemical properties of the membranes. Using RSM, the SCS-g-SPVA/PEO/SZrO₂-3C membrane's optimal ionic conductivity was 13.6 mS cm⁻¹, which was attained at the polynomial model's maximum point of 0.74 meq g⁻¹ for IEC, 92% water absorption, and almost 93% oxidative stability. The cost estimation for the prepared membranes is much lower than Nafion, which costs about 90 \$ m⁻², whereas the cost of the prepared membranes would not exceed 40 \$ m⁻².

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding authors.

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Author contributions

MHG proposed the project, wrote the manuscript with input from the other coauthors, and produced the membranes. NE performed the experiments, analyzed the data, and wrote the manuscript with input from the other coauthors. ME worked with MG in membrane fabrication. MAG, IR, and AH carried out different characterization tests. MY and DS supervised the work and revised the manuscript.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fmats.2022.912006/full#supplementary-material>

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