Preparation and characterization of sulfated zirconia (SO$_4^{2−}$/ZrO$_2$)/Nafion composite membranes for PEMFC operation at high temperature/low humidity

Yunfeng Zhaia,b, Huamin Zhang a,∗, Jingwei Hu a,b, Baolian Yia

* Proton Exchange Membrane Fuel Cell Key Materials and Technology Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457, Zhongshan Road, Dalian 116023, China
b Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

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Abstract
Fine particle superacidic sulfated zirconia (SO$_4^{2−}$/ZrO$_2$, S-ZrO$_2$) was synthesized by ameliorated method, and composite membranes with different S-ZrO$_2$ contents were prepared by a recasting procedure from a suspension of S-ZrO$_2$ powder and Nafion solution. The physico-chemical properties of the membranes were studied by ion exchange capacity (IEC) and liquid water uptake measurements, scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis, thermogravimetry–mass spectrometry (TG–MS) and Fourier transform infrared (FT-IR) spectroscopy. The results showed that the IEC of composite membrane increased with the content of S-ZrO$_2$, S-ZrO$_2$ was compatible with the Nafion matrix, the incorporation of the S-ZrO$_2$ could increase the crystallinity and also improve the initial degradation temperature of the composite membrane. The performance of single cell was the best when the S-ZrO$_2$ content was 15 wt.%, and achieved 1.35 W/cm$^2$ at 80 $^\circ$C and 0.99 W/cm$^2$ at 120 $^\circ$C based on H$_2$/O$_2$ and at a pressure of 2 atm, the performance of the single cell with optimized S-ZrO$_2$ was far more than that of the Nafion at the same condition (e.g. 1.28 W/cm$^2$ at 80 $^\circ$C, 0.75 W/cm$^2$ at 120 $^\circ$C). The 15 wt.% S-ZrO$_2$/Nafion composite membrane showed lower fuel cell internal resistance than Nafion membranes at high temperature and low relative humidity (RH).

Keywords: Sulfated zirconia, Composite membrane, S-ZrO$_2$/Nafion, High temperature PEMFC, Ion exchange capacity

1. Introduction
The proton exchange membrane fuel cells (PEMFCs) have been considered as one of the most promising clean energy technologies and suitable primary power source for transportation and stationary applications. The major advantages include: current prototype efficiency up to 64%, high energy densities and the ability to operate on clean fuels while emitting no pollutants [1]. Recently, more and more attention has been paid on high temperature PEMFC (>100 $^\circ$C) due to its faster electrode kinetics, greater tolerance to impurities in the fuel stream and easier water-thermal management [2]. Unfortunately, the proton conductivity of the typical membrane (Dupont’s Nafion series or other perfluorosulfonic acid (PFSA) membranes) decreases considerably at elevated temperatures due to the dehydration. In addition dehydration also results in membrane shrinkage and consequent poor contact between membrane and electrode [3]. The conventional PEM membranes are impossible to be used in high temperature PEMFC. Therefore it becomes essential to develop novel PEM membranes. For this purpose, different approaches have been developed: (i) modifying PFSA membranes to improve their water retention properties at temperatures above 100 $^\circ$C; (ii) modifying PFSA membranes to attain proton conduction independent of water; (iii) selecting new electrolytes based on solid state proton conducting materials [4]. Shao et al. [3], Adjemian et al. [5] and Tricoli and Nannetti [6] incorporated some inorganic materials (silica, zeolite, etc.) into PFSA membrane; Costamagna et al. [7], Yang et al. [4], Kim et al. [8] and Raman et al. [9] embedded proton conductivity materials (ZrP, CeHSO$_4$, ZrSPP, HPA, etc.) into PFSA membrane; other researchers Drishi et al. [10] and He et al. [11] investigated some novel heat-resistant
been reported that S-ZrO$_2$ exhibited a Hammett acid strength composite membranes with different S-ZrO$_2$ contents were prepared by a modified method, which was based on the method reported by Hara et al. [15]. Sulfated zirconia (S-ZrO$_2$) prepared by three different methods and found that it had a high conductivity of $2.3 \times 10^{-1}$ Sc m$^{-1}$ at 105–135 °C [15]. Thampan et al. had mentioned intermingling it into Naion for higher temperature composite PEM in his design for higher temperature composite PEMs [16].

In the present work, fine particles (less 0.5 μm) of sulfated zirconia (S-ZrO$_2$) were synthesized by ameliorated method, which was based on the method reported by Hara et al. [15]. Composite membranes with different S-ZrO$_2$ contents were prepared by evaporating the solvents from a suspension of S-ZrO$_2$ powder in a Naion solution. From our experimental results, compared with Naion membrane, the composite membrane exhibited higher cell performance, higher thermo-stability and fuel cell internal resistance at high temperatures and low relative humidity, so it is a very promising PEM material for high temperature PEMFC application.

2. Experimental

2.1. Preparation of S-ZrO$_2$ powder

The fine S-ZrO$_2$ powder was prepared by ameliorated method, which was based on the method reported by Hara et al. [15]. Zirconium oxychloride hydrate (ZrOCl$_2$·8H$_2$O), ammonia (NH$_4$·H$_2$O) and sulfuric acid (H$_2$SO$_4$) were used as starting materials, precipitating agent and sulfating agent, respectively. 28% NH$_4$·aq was gradually dropped into ZrOCl$_2$·8H$_2$O solution (0.20 M) and the pH value was adjusted to 10, hydrated zirconia (ZrO$_2$·nH$_2$O) hydrogel appeared. The obtained ZrO$_2$·nH$_2$O hydrogel was washed with distilled water using the centrifuge till no chloride ions were detected with silver nitrate (AgNO$_3$). The ZrO$_2$·nH$_2$O hydrogel was then changed into its alcogel by washing several times with anhydrous ethanol. The fine ZrO$_2$ powder was obtained by evaporating the solvents from a suspension of S-ZrO$_2$ prepared by evaporating the solvents from a suspension of S-ZrO$_2$ powder in a Naion solution. From our experimental results, compared with Naion membrane, the composite membrane exhibited higher cell performance, higher thermo-stability and fuel cell internal resistance at high temperatures and low relative humidity, so it is a very promising PEM material for high temperature PEMFC application.

2.2. Preparation of S-ZrO$_2$/Naion composite membranes

The composite membranes were prepared by the following procedure from 5 wt.% Naion solution (DuPont) with nominal equivalent weight (EW) of 1100. An appropriate amount of the Naion solution dried at 80 °C was dissolved in N,N-dimethylformamide (DMF) at 80 °C. Desired amount of S-ZrO$_2$ was added into the Naion/DMF solution, stirring vigorously for 30 min, and then treated in ultrasonic bath for 30 min to eliminate bubbles. The suspensions then were cast in glass trays with the designed dimensions, which were kept 12 h at 50 °C, and finally heated up to 160 °C for 2 h at a vacuum oven. Then, the recast composite membranes were detached from the glass trays by adding some de-ionized water. Finally, commercial Naion 112, the recast Naion and the composite membranes were purified by heating in the 5 wt.% hydrogen peroxide (H$_2$O$_2$) solution for 40 min, in 0.5 M H$_2$SO$_4$ for 40 min at 80 °C and in de-ionized water for 1 h at 100 °C, and dried 12 h at 100 °C, respectively. The composite membranes with 5, 10, 15, and 20 wt.% S-ZrO$_2$ and the recast Naion membrane (with 0 wt.% S-ZrO$_2$) were prepared, the thickness of all membranes was about 52 μm.

2.3. Physical and chemical characterization

The ion exchange capacity (IEC) indicates the number of milli-equivalents of ions in 1 g of the dry membrane. The IEC of S-ZrO$_2$ and membranes was measured by a classical titration method as following, specimens were soaked in excess 0.01 M NaOH solution for 48 h at ambient temperature, and then, the solution was titrated with 0.01 M HCl solution to an end point at pH=7.0 using neutral red indicator solution. The IEC of membranes was calculated via the relationship:

$$ \text{IEC} = \frac{m}{W_{\text{dry}}} \times 1000 $$

where IEC is the ion exchange capacity (mequiv/g), $n$ is the mole of NaOH or HCl, and $m$ is the dry sample mass (g).

The water uptake of membranes was measured by the following method. Specimens were boiled in distilled water 1 h, absorbed the water on the surface with filter paper and then dried 48 h at 105 °C, the water uptake of membranes was calculated via the relationship:

$$ W_{\%} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 $$

where $W_{\%}$ is the water uptake and $W_{\text{wet}}$ and $W_{\text{dry}}$ are the weights of the wet and dry samples (g), respectively.

The morphology of the 15 wt.% S-ZrO$_2$/Naion composite membrane was investigated using scanning electron microscope (JSM-6360LV, Japan) at 24 kV. The morphology included the size of the S-ZrO$_2$, uniformity of particle dispersion in the polymer matrix and compatibility between additive and polymer matrix.

The Dmax-RB diffractometer (Cu Ka radiation, at 40 kV/100 mA 0.1542 nm) was used to assess the crystallinity degree of the membranes before and after the embedment of the S-ZrO$_2$. In each case, the sample was placed on a glass slide and scanned in a range between 5° and 90° at a scan rate of 5°/min.

The attenuated total reflection (ATR) technique was performed using a FT-IR spectrometer (Avatar 370 E.S.P., Nicolet Continuum Infrared Microscope). The FT-IR spectra were recorded in the wave number range from 400 to 4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$, and the number of sample scans was 64. The KBr pellet method was used to measure the S-ZrO$_2$ powder.

The thermal stability and thermo-decomposition analysis were performed on a thermogravimetry–mass spectrometry
at the flow rate of 1.74 ml/min \( A \) (H\(_2\), utilization coefficient was with 2.6 mg/cm\(^2\) XC-72 carbon powder, and then a homogeneous mixture of 46.1 wt.% Pt/C catalysts (Tanaka) and 5 wt.% Nafion solution (DuPont) was sprayed onto it, with the loading of the dry Nafion resin about 0.6 mg/cm\(^2\). The Pt loading in the anode and cathode was 0.3 and 0.5 mg/cm\(^2\), respectively. The membrane was sandwiched between the anode and cathode, and then, it was warmed up for 60 s at 150 °C, 0.1 MPa and hot pressed for 90 s at 150 °C, 1 MPa. The geometrical area of the electrodes was about 5 cm\(^2\).

2.5. Measurement of single cell performance and internal resistance

The performance of single cell was evaluated at constant current E-load on a homemade fuel cell testing system, which could be referred to our previous reports \cite{17,18}. \( A \) (H\(_2\)) was used at the anode and O\(_2\) at the cathode, the gases outlet were controlled at the flow rate of 1.74 ml/min \( A \) (H\(_2\), utilization coefficient was 80%) and 3.5 ml/min \( A \) (O\(_2\), utilization coefficient was 50%). All data were obtained at a pressure of 0.2 MPa and temperature of water in the humidification bottles, which was determined by hygrometer (EE 30, E+E Elektronik GmbH). The resistance measurement was conducted using EG&G model 263A Potentiostate electrochemical working station at the open circuit condition. The test frequency was from 100 kHz to 100 mHz with logarithmic spacing, and the stimulate ac amplitude was 10 mV. The resistance measurements were conducted with the cell temperature at 80 and 120 °C, with varying relative humidity in the reactant gas of 10%, 20%, 40% and 60%. The relative humidity was manipulated by controlling the temperature of water in the humidification bottles, which was determined by hygrometer (EE 30, E+E Elektronik GmbH). The resistance was measured at the condition of N\(_2\) replacing O\(_2\) as cathode gas, and all date were collected only when the single cells testing system had been maintained stable for about 2 h.

3. Results and discussion

3.1. Ion-exchange capacity and water uptake of membranes

The IEC and water uptake of membranes are shown in Fig. 1. It shows that the IEC of Recast Nafion membrane is the same with that of Nafion 112, about 0.91 ± 0.01 mequiv/g, which is consistent with the value of Dupont, and there is an increase in IEC that is proportional to the amount of added S-ZrO\(_2\), but the maximum water uptake is at 10 wt.% content of S-ZrO\(_2\). The IEC of S-ZrO\(_2\) powder was also measured, about 1.91 ± 0.03 mequiv/g, and the expectation IEC of composite membranes was calculated based on the amounts of S-ZrO\(_2\) via the relationship: IEC = \( \sum \) \( i \) \( \times \) \( W_i \), \( W_i \) is the content in weight of Nafion or added S-ZrO\(_2\), as shown in Fig. 1, it can be seen that the experimental IECs agree with the calculated IECs. The possible reason for the increased IEC is that SO\(_4^{2-}\) on the surface of zirconia can provide Brønsted acid points that can be exchanged. The water uptake increase because that the presence of S-ZrO\(_2\) particles improves the mechanical properties of membranes when the content of S-ZrO\(_2\) is lower. But the weight increase makes against the water uptake, thus there is a decrease in water uptake when the content of S-ZrO\(_2\) is more than 10 wt.%. In the calculation of IEC, the IECs of S-ZrO\(_2\) were measured, about 1.91 mequiv/g, and the expectation IEC of composite membranes was calculated based on the amounts of S-ZrO\(_2\) via the relationship: IEC = \( \sum \) \( i \) \( \times \) \( W_i \), \( W_i \) is the content in weight of Nafion or added S-ZrO\(_2\), as shown in Fig. 1, it can be seen that the experimental IECs agree with the calculated IECs. The possible reason for the increased IEC is that SO\(_4^{2-}\) on the surface of zirconia can provide Brønsted acid points that can be exchanged. The water uptake increase because that the presence of S-ZrO\(_2\) particles improves the mechanical properties of membranes when the content of S-ZrO\(_2\) is lower. But the weight increase makes against the water uptake, thus there is a decrease in water uptake when the content of S-ZrO\(_2\) is more than 10 wt.%.

3.2. Microstructure of the composite membrane

The cross-section morphology of the 15 wt.% S-ZrO\(_2\)/Nafion composite membrane and the particle size distribution of S-ZrO\(_2\) are shown in Fig. 2. Fig. 2(a) shows that the S-ZrO\(_2\) particles are uniformly distributed over the membrane and no obvious agglomerate is found, the S-ZrO\(_2\) particles show good compatibility with polymer matrix. From Fig. 2(b), it can be seen that the sizes of S-ZrO\(_2\) particles are in the range 0.1–0.3 \( \mu \)m. These results indicate that the sizes of the S-ZrO\(_2\) particles are small enough to be uniformly distributed in the Nafion/DMF solution during casting and S-ZrO\(_2\) is compatible with Nafion matrix very well.

3.3. XRD analysis

The diffraction patterns of the S-ZrO\(_2\) powder and membranes are shown in Fig. 3. Both the recast Nafion and the composite membrane display a broad diffraction feature at 2\( \theta \) = 12–22°, which is in agreement with the reports of Moore.
The diffraction feature of S-ZrO$_2$ is consistent with that reported by Hara et al. [15]. The 15 wt.% S-ZrO$_2$ composite membrane also shows the diffraction feature of S-ZrO$_2$ powder. The broad peak (in Fig. 3) can be deconvoluted into two peaks (Fig. 4), which are assigned to amorphous ($2\theta = 16^\circ$) and crystalline ($2\theta = 17.5^\circ$) of polyfluorocarbon chains of Nafion, respectively according to Ref. [20]. Table 1 represents the areas of the deconvoluted peaks, centered at $2\theta \sim 15.9^\circ$ and $2\theta \sim 17.4^\circ$, and the ratio of crystalline phase. It can be seen that the crystallization degree of the composite membrane increases by 4.3%
Table 1
Crystalline phase content of membranes calculated from Fig. 4

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Area of the deconvoluted peak</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crystalline phase</td>
<td>Amorphous phase</td>
</tr>
<tr>
<td>Recast Nafion</td>
<td>240.9</td>
<td>1703.3</td>
</tr>
<tr>
<td>15 wt.% S-ZrO2/Nafion</td>
<td>439.25</td>
<td>2192.4</td>
</tr>
</tbody>
</table>

when 15 wt.% S-ZrO2 is mixed into it. The crystallization degree change is likely to be due to the altered ionomer chain mobility, influenced by the S-ZrO2 during the heat treatment of the samples above the glass transition temperature, \( T_g \) of Nafion.

3.4. FT-IR spectroscopy analysis

The FT-IR spectra of the S-ZrO2 and all the membranes are illustrated in Fig. 5. The major vibrational structures associated with the Nafion membrane are found in recast Nafion and the composite membrane. The peak at 1202 cm\(^{-1}\) is attributed to the stretching vibrations of \(-SO_3^-\) and \(-CF_2–CF_2–\), the peaks at 1150 and 1058 cm\(^{-1}\) to the stretching vibrations of \(-CF_2–CF_2–\), \(-SO_3^-\), respectively, and the peaks at 980 and 970 cm\(^{-1}\) to the stretching vibrations of \(-C–O–C–\), these are in agreement with the report of Falk[21]. In the FT-IR spectra of the S-ZrO2, the peak at 1630 cm\(^{-1}\) is attributed to the vibrations of acidic \(-OH\) groups, 748 cm\(^{-1}\) to the vibrations feature of ZrO2, and peaks at 1250, 1140 and 1041 cm\(^{-1}\) to the asymmetric stretching vibrations of sulfate groups binding via two oxygen atoms to the Zirconium of support, these also are reported in the literatures[15,22]. As regards the FT-IR spectra of the composite membrane, the peaks are at the same band position as the Nafion except that the band 1202 cm\(^{-1}\) shifts to 1216 cm\(^{-1}\), and it is stronger than that from Nafion membranes. These changes may be attributed to the interaction between S-ZrO2 and the polyfluorocarbon chains of Nafion. In addition, comparison of the peak area of \(-SO_3^-\) (at 1058 cm\(^{-1}\)) to that of \(-C–O–C–\) (at 980 and 970 cm\(^{-1}\)), it can be found that the content of \(-SO_3^-\) in composite membrane is about 7% higher than that in the recast Nafion membrane. This increase may be attributed to the SO4\(^{2-}\) in the S-ZrO2.

3.5. TG–MS analysis

The TG thermograms and the MS graphs of the S-ZrO2 are displayed in Fig. 6. It can be seen that the sample has a weight loss (about 2% loss) at temperature lower than 200 °C and more obvious weight loss (about 4.5% loss) in the range 600–900 °C. The ion currents, mass numbers of 48 and 64, have one peak between 600 and 900 °C, respectively. The first weight loss is due to the water evaporation from the surface of S-ZrO2 particles. According to the two peaks (mass numbers of 48 and 64 corresponding to SO2) in MS figure, the second one is due to the decomposition of SO4\(^{2-}\) bounded to the surface of ZrO2[15], which leads to the formation of SO2. The SO4\(^{2-}\) content in S-ZrO2 is estimated from weight loss to be about 4.5 wt.%.

The TG thermograms in Fig. 7 indicate that all the membranes retain more than 95% of their weights up to about 280 °C. Above 280 °C, the pure Nafion membranes started to decompose rapidly. By comparison, the composite membrane does not decompose until 300 °C. The weight loss of all membranes is about 9%. Upon further heating, all the membranes exhibit a second rapid decomposition range. Above 400 °C, the weight loss of pure Nafion membranes is about 83% and that of composite membrane is 66%. The composite membrane further goes through an additional weight loss about 5.2%, above 600 °C. The results of MS graphs (Fig. 8) are summarized in Table 2. The key fragments corresponding to the mass numbers are obtained according to literatures[23], which is displayed in Table 3. The first rapid weight loss of all membranes corresponds to the decomposition of side chains containing sulfonic acid group present in Nafion[23], producing SO2, CO2, HF and CF3COF. The second weight loss corresponds to the decomposition of carbon-fluorine backbone, the products involve COF2 besides above species. The decomposition temperature of Nafion...
Table 2
The peaks of ion current at different temperatures from Fig. 8

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Temperature (°C)</th>
<th>Mass numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recast Nafion</td>
<td>260</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>64, 48, 44, 20, 47, 69, 50</td>
</tr>
<tr>
<td></td>
<td>410</td>
<td>64, 48, 67, 67</td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>44, 69, 20, 50, 31, 81</td>
</tr>
<tr>
<td></td>
<td>470</td>
<td>44, 20, 50, 69, 47, 81, 31</td>
</tr>
<tr>
<td></td>
<td>620</td>
<td>44</td>
</tr>
<tr>
<td>Composite membrane</td>
<td>280</td>
<td>81, 47</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>64, 48, 44, 31, 69, 47, 20, 50</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>44, 64, 48, 47, 67</td>
</tr>
<tr>
<td></td>
<td>470</td>
<td>44, 20, 31, 69, 50, 47, 81</td>
</tr>
<tr>
<td></td>
<td>510</td>
<td>44, 20</td>
</tr>
<tr>
<td></td>
<td>620</td>
<td>44, 20</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>44, 20</td>
</tr>
</tbody>
</table>

Increases due to the presence of the S-ZrO₂. The last weight loss of composite membrane (Fig. 7) involves that of the S-ZrO₂, but it is larger than that of S-ZrO₂ itself (Fig. 6), because it includes the additional exhaust of CO₂ and HF. Considering the shift of the band 1202–1216 cm⁻¹ of FT-IR pattern (Fig. 5), it is assumed that there may be some chemical reaction between the polyfluorocarbon chains of Nafion and the S-ZrO₂, which awaits our further study.

3.6. Performance and Internal resistance of single cells

The polarization and power density curves of the single cells with Nafion 112, recast Nafion membrane and 15 wt.% S-ZrO₂/Nafion composite membrane obtained on H₂/O₂ at 80 °C (gases saturated at 80 °C, RH ≈1) and 120 °C (gases saturated at 110 °C, RH=0.6) are shown in Fig. 9. These curves were recorded on our homemade fuel cell testing system, with the inlet pressure of \( P_{\text{H}_2} = P_{\text{O}_2} = 0.2 \text{ MPa}. \) Fig. 9(a) suggests that when operated at normal operational temperature, the optimal S-ZrO₂ content in composite membrane is 15 wt.%, the cell performance with 15 wt.% S-ZrO₂/Nafion composite membrane reaches 1.35 W/cm², which is superior to the single cell performance with Nafion 112 (1.22 W/cm²) and recast Nafion (1.28 W/cm²). From Fig. 9(b), it is obvious that at higher operational temperatures (120 °C), the performance of cells with composite membranes is higher than that with Nafton 112 (0.75 W/cm²) and recast Nafion membrane (0.72 W/cm²), also the cell with 15 wt.% S-ZrO₂/Nafion composite membrane gives the best performance (0.99 W/cm²). It should be noted that, when the S-ZrO₂ content is 15 wt.%, the single cell shows the best performance at both 80 and 120 °C, as it is shown in Fig. 1, 15 wt.% is the optimum content when considering the water uptake and ICE simultaneously. The polarization curves of the single cells at 120 °C and different RH are shown in Fig. 10. It can be seen that the performances and the open current voltage of cells increase with the increase of RH. 15 wt.% S-ZrO₂/Nafion composite membrane shows a higher cell performance than Nafion 112 and recast Nafton membrane at all the RH researched in this work.

The internal resistances of the single cells at different temperatures obtained by ac impedance are displayed as a function of...
Table 3
The key fragments corresponding to the ion currents in Table 2

<table>
<thead>
<tr>
<th>Mass numbers</th>
<th>20</th>
<th>44</th>
<th>67</th>
<th>81</th>
<th>48</th>
<th>64</th>
<th>31</th>
<th>50</th>
<th>69</th>
<th>47</th>
</tr>
</thead>
<tbody>
<tr>
<td>Key fragments</td>
<td>HF$^+$</td>
<td>CO$_2^+$</td>
<td>COF$_2^+$</td>
<td>SO$_3^+$</td>
<td>SO$_2^+$</td>
<td>CF$^+$</td>
<td>CF$_2^+$</td>
<td>CF$_3^+$</td>
<td>COF$^+$</td>
<td></td>
</tr>
<tr>
<td>Probable molecules</td>
<td>HF</td>
<td>CO$_2$</td>
<td>COF$_2$</td>
<td>H$_2$SO$_3$</td>
<td>SO$_2$</td>
<td>CF$_3$COF</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

RH in Fig. 11, which can reflect the influence of RH on the conductivity of membranes at the same electrode condition. The 15 wt.% S-ZrO$_2$/Nafion membrane is chosen because it gave the best performance in single cell. From Fig. 11, it can be seen that the composite membrane displays high conductivity at high temperature/low RH, the influence of RH on the conductivity of Nafion 112 is more obvious. It can be observed that the influence of RH on the conductivity of all membranes is more obvious when the cell is operated at higher temperature or lower RH. All the experimental results are reproducible, and it indicates that the novel composite membrane is a very promising material for high temperature PEMFC application.

![Figure 11](image1)

Fig. 9. The performance of single cells with Nafion 112, recast Nafion and 15 wt.% S-ZrO$_2$/Nafion membranes: (a) 80°C (gases saturated at 80°C, RH=0); (b) 120°C (gases saturated at 110°C, RH=0.6), $P_H=0.2$ MPa.

Fig. 10. The polarization curves of single cells with Nafion 112, recast Nafion and 15 wt.% S-ZrO$_2$/Nafion membranes at 120°C: RH=0.1, 0.4 and 0.6.

![Figure 10](image2)

Fig. 11. The internal resistances of single cells: (▲, △) Nafion 112, (▽) 15 wt.% S-ZrO$_2$/Nafion.

4. Conclusions

The fine powder of sulfated zirconia (SO$_4^{2-}$/ZrO$_2$, S-ZrO$_2$) was synthesized by ameliorated method and the composite membranes with different S-ZrO$_2$ contents were prepared by a recasting procedure. The IEC increases with increasing of the amount of added S-ZrO$_2$, and the water uptake reaches to maximum when the content is 10 wt.%. The S-ZrO$_2$ powder is uniformly distributed throughout the composite membrane. The crystallization degree and the content of SO$_4^{2-}$ of the composite
membrane increase. The single cell performance test and internal resistance measurement show that the S-ZrO\textsubscript{2} composite membrane gives better performance, especially when the S-ZrO\textsubscript{2} content is 15 wt.%. Therefore, the composite membrane is a very promising membrane material for PEMFC operation at higher temperature and lower humidity.

References


