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Short Communication

Charge Transport Improvement in Nafion Membrane by Simoultaneous Microwave Synthesis and Deposition of YSZ

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The improvement of water retention properties of Nafion membranes is a key feature that could simplify its operation and increase the reliability of Proton Exchange Membrane Fuel Cells (PEMFC). In this work, nanostructured YSZ was synthesized in a microwave reactor and their properties were evaluated by TEM and XRD. After characterization, YSZ was deposited on Nafion membranes by three different methods, including a novel simultaneous YSZ synthesis/deposition on Nafion as an attempt to simplify the process and to improve the effectiveness of the deposition of the material in the membrane. The water retention properties of the modified membranes were evaluated and compared with un-modified Nafion. Their electrochemical properties were characterized by Electrochemical Impedance Spectroscopy (EIS) to determine the relationship between the YSZ deposition, the water retention and its protonic charge conductivity. The evaluations have shown that membranes modified with YZS exhibited higher water retention. Furthermore, the YSZ modified membranes showed an important diminution in their charge transfer resistance compared to commercial Nafion.

Keywords: YSZ; Nafion charge transport; EIS characterization; PEMFC

1. INTRODUCTION

Proton Exchange Membrane Fuel Cells (PEMFC) are high efficiency and low environmental impact energy conversion devices [1,2]. In a PEMFC, hydrogen and oxygen are supplied to the cell, where the fuel is split into protons (H^+) and electrons. Electrons are driven outside the system and the protons are transported by the polymer electrolyte to the cathode whereby the circuit is closed [1]. Currently, due to their attractive chemical and mechanical properties, DuPont's Nafion membrane is one of the most widely used polymer electrolyte in PEMFC [3-5]. Despite their advantageous characteristics, Nafion conductivity at low hydration levels is still an issue that limits the PEMFC current density and compromises cell's efficiency and performance.

Several models have been developed to achieve a complete understanding of the protonic charge transport in Nafion membrane and its water dependence. Ise and Kreuer based on a SAXS analysis generated until now the most accepted schematic representation of Nafion [6,7]. Their results combined with the initially proposed Grotthuss mechanism [8,9] and the introduction of the Zundel ($H_5O_2^+$) and Eigen ($H_9O_5^+$) ions in Nafion nano-channels structure [7,10] established a consistent relationship between the membrane's hydration level and the phenomena observed in the protonic charge transport in Nafion membranes [9,10].

Because of this close relationship between Nafion conductivity and its hydration level, the proper operation of PEMFCs demands the implementation of humidification and water management systems, increasing the cost and complexity of PEMFC and affecting its portability. Several strategies have been attempted in order to increase water retention and hence conductivity in Nafion membrane. Some methods include the incorporation of heteropolyacids such as phosphotungstic and molybdophosphoric acid [11,12], or the incorporation of non-aqueous solvents as the primary proton carrier [13-15]. Nevertheless, these strategies have been unsuccessful at medium and long-term operation, mainly because of the leaching of these additives from the membrane. In order to prevent the latter, water retention can also be increased by the incorporation of highly hydrophilic oxides into the Nafion structure. Some of these filling compounds include SO_2, TiO_2, and ZrO_2/Y_2O_3 (YSZ) [16-23]. YSZ is one of the most attractive candidates as filling material for Nafion in PEMFC, not only because of its high hydrophilicity and thermal stability but also due to its intrinsic protonic conduction [24-26]. Usually, YSZ is incorporated into the membrane's matrix by the Sol-Gel method, where the host proton exchange membrane is used as a template to direct the morphology and particle size of the oxide in the PEM structure [20,22,24]. As a strategy to simplify the YSZ incorporation, in this work, YSZ was first synthesized in a microwave assisted reactor and their physical properties were determined by TEM and XRD analysis, then three different deposition methods were evaluated to determine the YSZ load in the membrane and its relation with the water uptake and electrochemical response.

2. MATERIALS AND METHODS

This section presents the detailed explanation of the experimental procedure performed for nanostructured YSZ synthesis and its deposition over Nafion as well as the details for their physical and electrochemical evaluation.

2.1 Synthesis of YSZ

The yttrium and zirconium oxides were prepared using the precursors, yttrium (III) chloride (anhydrous powder 99.99% Aldrich), zirconium (IV) chloride (anhydrous powder 99.99% Aldrich), sodium ethoxide (≥95%, Aldrich) and ethanol (99.9% Fermont). All the reactants were used as received without any treatment or purification.

Two different solutions of $ZrCl_4$ and YCl_3 were prepared by dissolving the proper amount of precursors in 5 ml of ethanol for each compound until concentrations of 0.25 M and 0.04 M were reached for $ZrCl_4$ and YCl_3 respectively. After the precursors were stirred and dissolved, both solutions were mixed together to obtain 10 ml of a homogeneous solution of $ZrCl_4$ and YCl_3 in ethanol. Separately, the sodium ethoxide was dissolved in 10 ml of ethanol to obtain a 1 M solution. Afterwards, the sodium ethoxide was incorporated drop by drop in the zirconium and yttrium chloride solution and stirred for 1 hr at room temperature and then placed in the microwave system (Synthos 3000 Anton Paar) at 1000 W, 160°C and 28 bar during 10 min to accomplish the desired reactions for the YSZ synthesis.

After the sol-gel solution of YSZ was obtained, the solids were separated by centrifugation, ultrasonic cleaning and decantation. This process was performed twice in order to remove any undesirable byproducts. Finally, the powder was dried at room temperature and the properties of the resulting YSZ were determined by XRD and TEM.

2.2 XRD and TEM Characterization

The crystallographic analysis for YSZ was performed with Cu kα X-ray radiation produced in a Rigaku DMAX 2200 X-ray machine operating at 40 kV and 30 mA. The XRD patterns were obtained at a scanning rate of 1°/min with a step size in the 2θ scan of 0.02° and in the range 1-70°. The TEM micrographs were obtained in a JEOL JEM-2010 operating at 200 kV and 115 μA with a camera length of 20 cm, the average particle size for YSZ was calculated by counting 150 particles.

2.3 Incorporation of YSZ into Nafion by Three Different Methods

Before the YSZ deposition, all the membranes were purified during 30 min in 3% of H_2O_2 at 85°C and then activated in 1 M H_2SO_4 at 85° C for 1 hr [27]. After activation, three modification methods were employed to incorporate the YSZ into the Nafion structure, which are described below.

2.3.1. Dry Deposit and MeOH Deposit on Membranes

One membrane was dried in an electric oven under air atmosphere at 80°C during 72 hrs (Dry Deposit sample), while the other was immersed in a solution of methanol and deionized water under stirring (5:1 in volume) at room temperature during 24 hrs (MeOH Deposit sample). After that, both membranes were placed in a solution of YSZ in water (500 mg of powder in 100 ml of deionized water) and stirred during 3 hrs. Then the membranes were rinsed with 2-propanol to remove any excess of material from the surface, dried in air during 48 hrs in an oven at 100°C and once again activated [28,29].

2.3.2. Simultaneous YSZ Synthesis and Deposition

In this method the activated membrane was modified at the same time that the YSZ is synthesized in the microwave assisted synthesis reactor. The membrane (simultaneous sample) was placed in the reaction vessel along with the precursor solution described above. The temperature was set at 120°C at 800 W during 20 minutes. After that, the membrane was rinsed with methanol and newly activated.

2.3.3. Water Absorption Determination

To evaluate the water absorption capacity of commercial and YSZ modified Nafion, the membranes were dried at 150°C in air in an electric oven for 20 hrs and weighed in an analytical balance (OHAUS EP214C Explorer Pro); then the membranes were immersed in de-ionized water for 24 hrs, removed from water and then placed between tissue papers to remove the excess of water and weighed again. This procedure was repeated in three different samples and the average values are reported. The water uptake (U) was calculated using the weights of wet (W_W) and dry membrane (W_D) according to the following formula:

$$U(\%) = \frac{W_W - W_D}{W_D}.100 \qquad 1$$

2.4 EIS characterization

After activation, the membranes were stored in de-ionized water during 24 hrs, and then dried with paper and their electrochemical characteristics were evaluated by the 4-electrode method [30]. The EIS evaluations were obtained applying a 10 mV sinusoidal wave in a frequency range from 100 kHz to 10 mHz at 25°C. The experimental impedance data was simulated with Electrical Equivalent Circuits (EEC) using the ZVIEW software in order to determine the values for the membrane protonic charge resistance.

3. RESULTS AND DISCUSSION

3.1 Characterization of YSZ

Figure 1 shows the x-ray diffractogram for the as-prepared YSZ. A cubic structure (PDF#82-1246) with low crystallinity and with a lattice parameter of 5.14728 Å was observed for the material, which can be seen in figure 1.

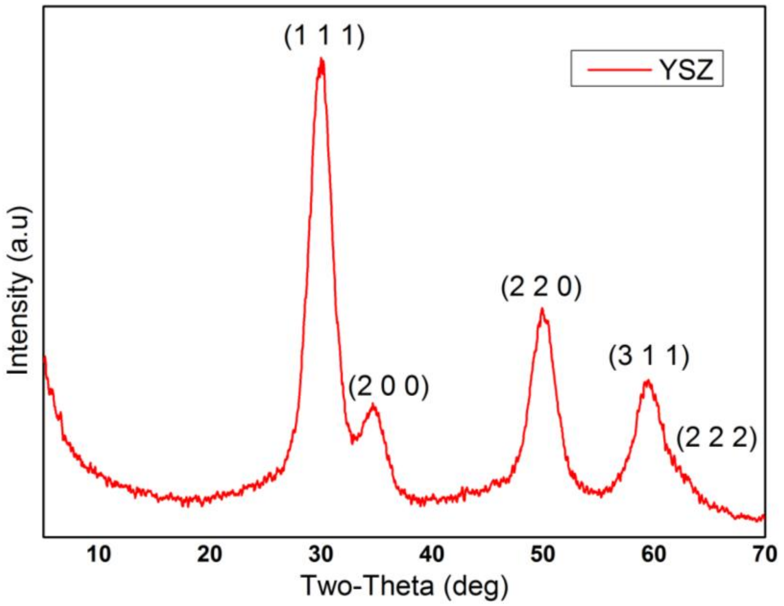

Figure 1. X-ray diffractogram for the as-prepared YSZ

The YSZ was analyzed by TEM in a Jeol JEM-2010 microscope at 200 kV. Equation 2 was used for the diffraction pattern indexing, which is shown in figure 2, where d is the interatomic distance, R the distance between reflections, λ the wavelength and L the camera length.

$$d = \frac{\lambda \times L}{R} \qquad 2$$

The rings shown in the electron diffraction pattern in figure 2 correspond to the interplanar distances related to a nanostructured, face-centered cubic phase of yttria stabilized zirconia polycrystalline structure.

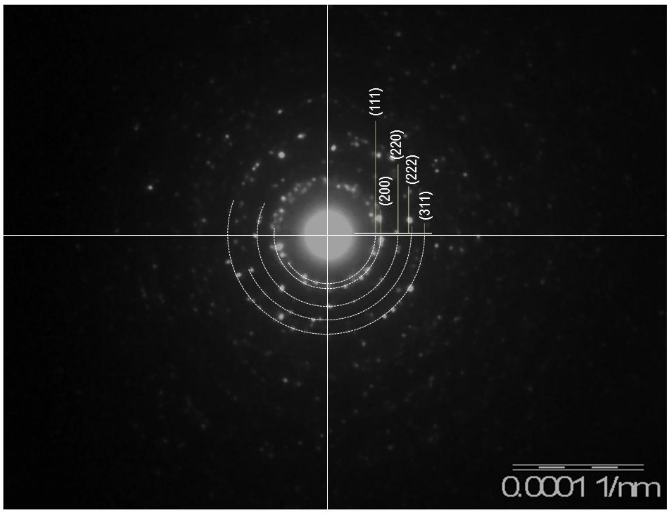

Figure 2. Electron diffraction pattern corresponding to the YSZ obtained by microwave assisted synthesis.

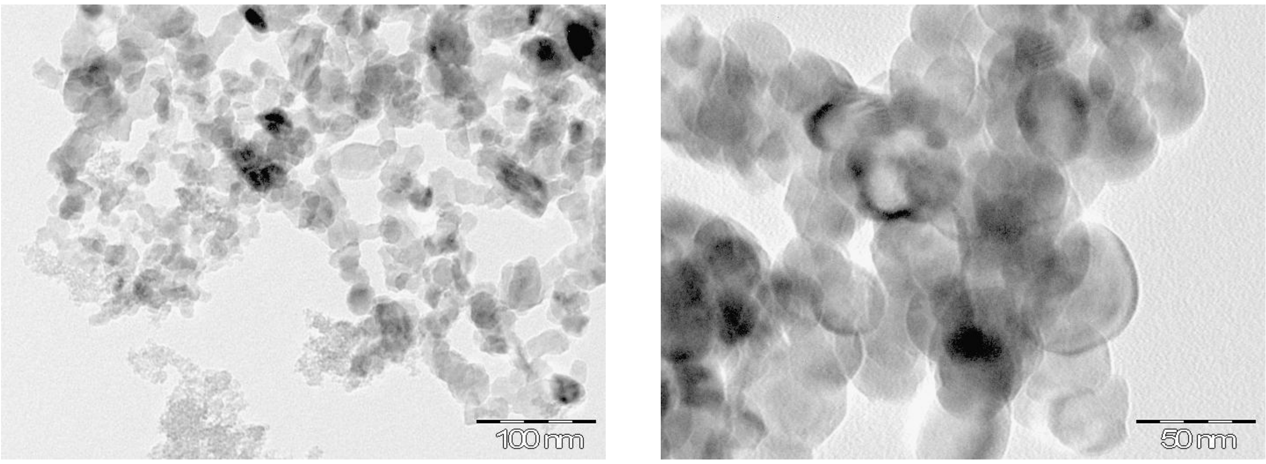

Figure 3. TEM micrographs obtained at different magnifications for YSZ.

The YSZ synthesis produced irregular shape nanometric particles with an average size less than 40 nm with some smaller particles forming agglomerations as observed in figures 3a and 3b.

3.2 Water Absorption Capacity

The absorption capacity and water retention are the main parameters related with Nafion ionic conductivity [9,10]. The unmodified Nafion and the membranes modified with YSZ were evaluated to determine the water absorption as a weight difference between the dry and hydrated membrane.

Table 1. Water absorption of modified YSZ membranes compared to commercial Nafion.

Sample	W_W (mg)	W_D (mg)	Absorption of H_2O U (%)
Nafion	43.4	34.6	25.43
Simultaneous	117.5	68.8	41.44
MeOH Deposit	78.1	57.2	36.53
Dry Deposit	58.9	44.9	31.18

As shown in table 1 all the YSZ modified membranes exhibited an important increase in its water absorption capacity compared to commercial Nafion. When the dry mass of membranes is compared, it is possible to say that the modification processes that allowed depositing larger YSZ quantities (simultaneous sample) resulted also in membranes with higher water absorption capacity due to the water retention properties of YSZ. Similar results were obtained when analyzing membranes doped with other metal oxides such as SiO_2, ZrO_2 and TiO_2; nevertheless, those membranes exhibited poor durability due to leaching and electrochemical reduction, combined with an overall decrease in protonic charge conductivity because of the addition of non-conductive oxides. [31-34]

3.3 EIS analysis

The EIS results are shown in the Nyquist plots of figure 4. Each membrane is represented by two overlapped semicircles associated with the relaxation processes of two different conduction processes. Initially, the protonic charge should be transferred from the membrane´s surface to its structure and is represented by the Diffusion Boundary Layer (DBL), followed by the charge transport through a Heterogeneous Ionic Transference (HIT) inside the Nafion structure [30,35,36]. The EEC used in the simulation is shown in figure 5 and the circuit element values listed in table 2. It can be noticed that due to the semicircle depression observed in Nyquist plots (figure 4), Constant Phase Elements (CPE) had to be used to simulate the capacitive response. This is a behavior typically found in rough surfaces with a heterogeneous current flow such as Nafion membranes [37].

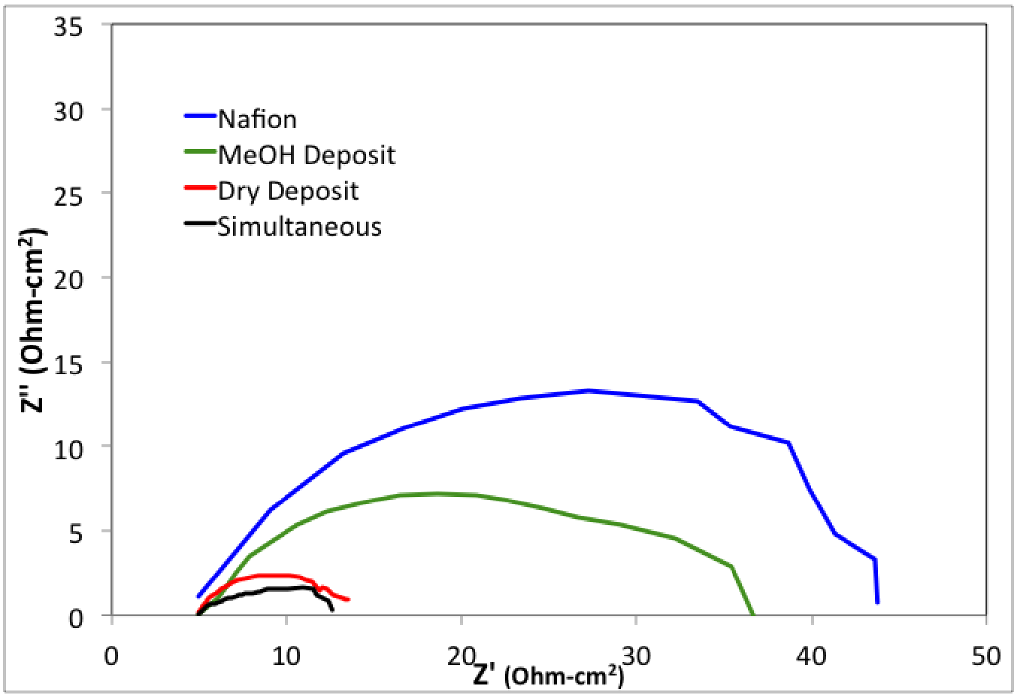

Figure 4. The EIS spectra (Nyquist plot) for commercial and modified YSZ membranes

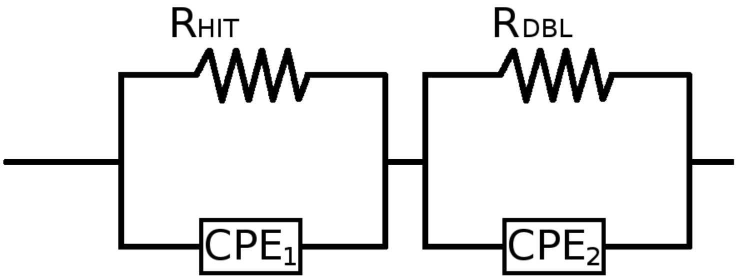

Figure 5. The EEC used to simulate the EIS data, where capacitors where substituted by Constant Phase Elements.

When analyzing from right to left the EECs in figure 4, the first R-CPE low frequency couple corresponds to the protonic charge transference process in the outer DBL. The resistance and CPE values are associated with the difficulty or easiness for protonic charge to be transferred from the interface to the Nafion structure; followed by the opposition faced in the Nafion bulk and represented by the high frequency R-CPE couple on the left, while the total protonic charge resistance is summarized in the Charge Transfer Resistance (R_{CT}) presented in the first column of table 2.

Table 2. Values of the equivalent electrical circuits obtained by simulation of the EIS data.

	R_{CT} (Ω)	R_{DBL} (Ω)	R_{HIT} (Ω)	CPE_1 (F)	P_1	CPE_2 (F)	P_2
Nafion	39	29	10	5.0E-06	0.86	9.0E-06	0.88
MeOH Deposit	33	12	21	1.6E-04	0.50	1.0E-06	0.80
Dry Deposit	8.8	7.38	1.47	7.4E-03	0.98	2.8E-05	1.00
Simultaneous	7.8	5.08	2.8	3.9E-04	0.52	2.8E-05	0.70

According to the plots and the R_{CT} values obtained, all the YSZ modified membranes exhibited an important decrease in its ionic resistance. From 39 Ω for unmodified Nafion to a minimum of 7.8 Ω for the membrane simultaneously modified under the microwave assisted synthesis. Furthermore, almost all the samples exhibited a typical Nafion/electrode response that can be observed in higher values for the R_{DBL} compared to the R_{HIT}. Only the MeOH deposited sample showed a R_{HIT} value higher than the R_{DBL}. This behavior is atypical of Nafion and can only be attributed to modifications in its internal structure such as channel narrowing or blocking because of the addition of the dopant materials [38].

4. CONCLUSIONS & RECOMMENDATIONS

The protonic charge transfer in Nafion membrane is directly related to its water retention properties. In this work, it has been proved that the addition of nanostructured YSZ to Nafion membranes increased its water retention and hence the charge transport capacity because of the hydrophilic properties of YSZ. The EIS evaluations showed that YSZ modified membranes exhibited a higher protonic charge conductivity compared to commercial Nafion.

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