Temperature-Dependent Conductivity of Nickel-Based Anion-Exchange Membrane Fuel Cell

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Abstract

In this letter, a simple and low-cost design of a nickel-based anion-exchange membrane fuel cell is proposed. The temperature-dependent conductivity of a nickel-based anion-exchange membrane fuel cell is studied. The adsorption of CO_2 on the membrane surface is also determined as a function of operation temperature. Results showed that the conductivity of the membrane reasonably depends on its type, structural purity, and temperature. The hydroxide (OH^-) ions showed stable and high conductivity up to 305 mS/cm after 20 hours of operation, whereas the HCO_3^- ions showed unstable and low conductivity due to their larger size. The adsorption of CO_2 on the membrane surface was reduced at elevated temperatures, which limits the conversion of OH^- ions into HCO_3^- ions as well as enhances the overall performance of the cell.

Keywords: Anion-exchange membrane; Fuel cells; Nickel compounds; Electrical conductivity
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1. Introduction

The nickel-based anion-exchange membrane (AEM) fuel cells are promising technology for clean energy conversion as they provide low-cost high-efficient alternatives for the conventional systems based on noble metals [1,2]. The performance of these cells fundamentally depends on the electrochemical properties of the nickel-based catalysts those may show large variations with variable operating temperature [3,4]. This makes the understanding of the temperature-dependent conductivity very important to enhance such performance as the temperature has direct effect on the reaction kinetics inside the fuel cell [5,6]. In general, increasing temperature leads to accelerate the rates of oxygen reduction reaction at the cathode as well as the fuel oxidation reaction at the anode throughout providing sufficient activation energy to overcome the energy barriers [7,8]. For nickel-based catalysts, this effect is tightly related to the variation in the density of states of nickel surface because the density of electronic states near Fermi level increases at elevated temperatures, which facilitates the transfer of electrons between catalyst and reactants, and hence enhances the catalytic performance [9,10]. However, a main challenge facing these catalysts is the oxidation of nickel surface and formation of passivation layers, such as $Ni(OH)_2$ or NiO, which hinder the electronic conductivity and limit the catalytic activity [11,12]. The formation dynamics of these layers is reasonably affected by temperature because the moderate temperatures may lead to support the formation of a chemically-active phase whereas the high temperatures lead to undesired oxidation and hence performance degradation [13,14]. Furthermore, the effect of temperature may include the anion-exchange membrane because the ionic conductivity through the membrane largely depends on the water content and ionic dynamics [15]. Increasing temperature results in supporting the dynamics of hydroxide ions (OH^-) through the membrane, which enhances the overall ionic conductivity. However, this should be compensated with the risk of membrane dehydration at very high temperatures as the Ohmic resistance is consequently increased and the cell efficiency is decreased [16]. Also, the reaction between the nickel-based catalyst and membrane at elevated temperatures may cause variations at the catalyst-membrane interface that affects the electric contact and ionic distribution [17].

The morphological properties of nickel nanoparticles, such as particle size distribution and effective surface area, are also affected by heat exposure as the elevated temperatures may cause particle agglomeration, reduction in the effective surface area, and accordingly, reduce the number of active sites available for reaction [18,19]. Therefore, to understand the complex relation between temperature and conductivity in nickel-based fuel cells, a comprehensive study combining the analysis of nickel electronic properties, the formation dynamics of surface oxides, the behavior of ion transportation in the membrane, and thermal stability of materials, in order to determine the optimum temperature window that achieve the maximum benefit from dynamically accelerated reactions and avoid degradation mechanisms [20-22]. This would prepare to develop much more sustainable and economic energy systems based on abundant catalysts, such as nickel, instead of precious or noble metals.

In this letter, the temperature-dependent conductivity of a nickel-based anion-exchange membrane fuel cell is studied. The adsorption of CO_2 on the membrane surface is also determined as a function of operation temperature.

2. Experimental Part

Figure (1) shows schematically the design of the AEM fuel cell. Such eco-friendly design can show good capability to operate at lower harsh environments when compared to other designs and types of fuel cells. In this design, the cathode is fed with oxygen while the anode is fed with pure hydrogen, which is oxidized at the cathode with the assist of the catalyst to split the hydrogen molecule into two atoms, each of them is converted into a proton and an electron. Due to the alkaline nature of this cell, the resulted protons immediately react with hydroxyl ions (OH^-) coming from the cathode through the membrane to form water molecules at the anode and free electrons to pass though the external circuit and produce current. In existence of these electrons, oxygen react with water to form the hydroxyl ions (OH^-) those represent the base to operate such cells. These OH^- ions transport through the membrane towards the anode, and this is why this membrane is called anion-exchange because it allows negative ions only to pass though.

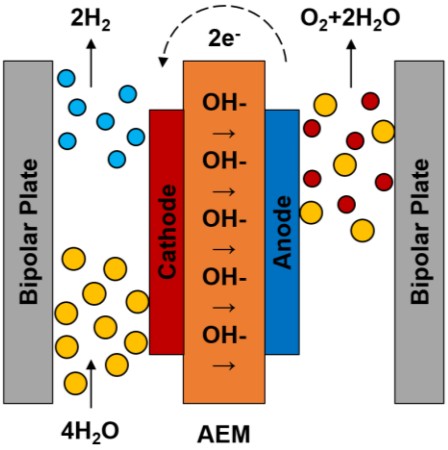


Fig. (1) Schematic diagram of the AEM fuel cell considered in this work

The bipolar plates on both sides of the cell have a crucial role in collecting the current resulted from electrons as well as distribute the gases (hydrogen and oxygen) evenly over the porous electrodes. These plates can cool the cell, separate the individual cells and stack them to produce higher potentials and currents. By the mechanisms mentioned above, the overall reactions consume the OH^- ions at the anode and produce them on the cathode. This maintains continuous flow of these ions through the membrane to balance the charge and internally close the circuit.

The most important feature of the proposed design of AEM fuel cell is the possibility to use nickel or cobalt instead of platinum, especially of the alkaline side. This reasonably reduces the overall cost of the cell. The flow direction of ions from the cathode to anode assists in limiting the problem of water accumulation and flooding that may occur in other types of fuel cells. Accordingly, this cell proposes a promising solution to produce clean energy since its only outcome is water and heat. Therefore, it can be considered as an ideal technology for stationary and mobile applications evenly.

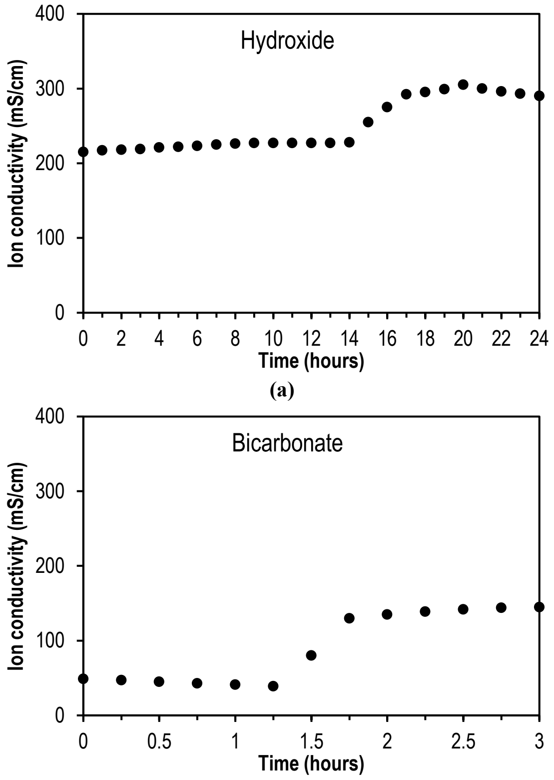
3. Results and Discussion

Figure (2) shows the conductivity as a function of time for hydroxide (OH^-) and bicarbonate (HCO_3^-) ions in the AEM fuel cell proposed in this work. In Fig. (2a), a dynamic behavior is observed over time durations up to 24 hours. The conductivity is initially low, reaching its maximum (~305 mS/cm) after 20 hours of operation to represent a relative high and stable operation. This behavior expresses a gradual activation process in the membrane over time as the high-mobile OH^- ion needs enough time to adsorb the humidity and form effective conductive channels within the structure of the membrane. The increase and then stability of conductivity reveal the success of nickel-based membrane to maintain its chemical and physical stability under alkaline operational conditions. This is very important for practical applications requiring long-range sustainable operation.

On the other hand, figure (2b) shows totally different behavior of the conductivity of HCO_3^- ions measured over short-range duration not longer than 3 hours. After half an hour, the conductivity is about 45 mS/cm, decreases slightly, and then rises to about 135 mS/cm after 2 hours. This behavior is attributed to the different chemical nature of HCO_3^- ion, as its larger size and distributed charge reduce its ability to move through the membrane structure when compared to the OH^- ion (smaller and faster) [23]. Moreover, the rapid decrease in conductivity refers to the possibility of HCO_3^- ions reaction with the effective components of the membrane and conversion to other forms, such as CO_3^{2-} of lower conductivity, or to the unstable membrane structure when exposed to these ions, which may cause structural degradation over time [24].

The comparison between two curves indicates a highly importance to select operation conditions those are appropriate for fuel cells based on nickel AEM. While the OH^- ions provide higher and stable conductivity, which makes them the optimum choice for practical applications, the conversion of these ions into bicarbonate under normal atmospheric conditions due to their reaction with CO_2 in the air represents a big challenge.

In materials engineering, the design of nickel-based membranes with capability to resist the effects of bicarbonate or to maintain moderate conductivity can be seen as a strategic research goal. The solution can be obtained by the modification of membrane structure to create much more selective ionic channels or develop composite membranes containing nanomaterials to enhance the conductivity even though larger ions are existing [25].



(a)

(b)

Fig. (2) Conductivity as a function of operation time for (a) OH^- ions, and (b) HCO_3^- ions

Figure (3) shows an inverse relationship between operation temperature and the CO_2 amount adsorbed on the membrane surface. This amount was decreased from 119 to 10 µmol/g as the temperature was increased from 0 to 120 °C. This behavior is very crucial when studying the conductivity of OH^- ions in alkaline fuel cells as the conversion of these high-conductive ions into low-conductive HCO_3^- ions or carbonate is limited. This result partially interprets the enhanced electrochemical performance of the cell at elevated temperatures because the membrane maintains its ionic purity and hence reduces the carbon poisoning effect.

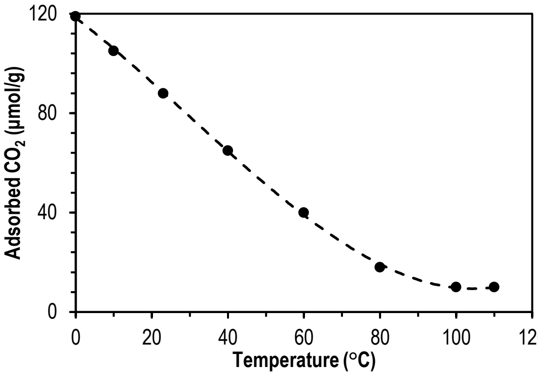


Fig. (3) CO_2 adsorption on the membrane surface as a function of operation temperature

4. Conclusion

The big difference in the behaviors of conductivity of these ions over time confirms the significance to perform temperature-dependent studies to deeply understand the ionic transport mechanisms. The activation of ion distribution through the membrane requires different energies according to the type and chemical structure of the ion. Elevated temperatures may lead to enhance the mobility of bicarbonate ions or change the reaction mechanisms within the membrane. This may explore new advantages to use these fuel cells in CO_2-rich environments while the efficiency is maintained.

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