A high-performance integrated electrode for anion-exchange membrane direct ethanol fuel cells

Y.S. Li, T.S. Zhao*

Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China

A B S T R A C T

We propose a new anode electrode structure that is composed of a nickel foam layer with thin catalyst films coated onto the skeleton of the foam. This innovative design of the anode electrode enables the integration of the catalyst and diffusion layers, thereby extending the electrochemical active surface area and facilitating the transport of species. The experimental results indicate that the use of the integrated electrode in an anion-exchange membrane direct ethanol fuel cell can significantly improve the cell performance as compared with the use of the conventional electrode that has separated catalyst and diffusion layers; a peak power density of 130 mW cm\(^{-2}\) and a maximum current density of 1060 mA cm\(^{-2}\) are achieved at 80 °C.

1. Introduction

Direct alcohol fuel cells (DAFCs) that directly convert the chemical energy stored in the alcohol into electricity make it promising as an environment-friendly power source for portable and mobile applications [1–3]. Among various alcohol fuels, ethanol is less toxic and can be massively produced from agricultural products or biomass, in addition to the advantage of high-specific energy. Hence, tremendous efforts have been made to the development of direct ethanol fuel cells (DEFCs), including both proton-exchange membrane (PEM) and anion-exchange membrane (AEM) DEFCs [4–7]. However, conventional PEM DEFCs that use a platinum-based catalyst have demonstrated extremely poor performance, primarily because it is difficult to oxidize ethanol in an acid medium. On the other hand, however, as the alkaline environment in AEM DEFCs speeds up the electro-kinetics of both the ethanol oxidation reaction (EOR) and oxygen reduction reaction (ORR), AEM DEFCs can yield much higher performance than PEM DEFCs, even with low-cost non-Pt metals as the electro-catalyst. Moreover, liquid-feed AEM DEFCs also possess the advantages that a direct methanol fuel cell (DMFC) has, including simpler system structures, high-specific energy and fast refueling. Because of the above-mentioned important features, AEM DEFCs have recently attracted increasing attention [8–11].

Over the past decade, effort has mainly been focused on the development of materials for AEM DEFCs, including anion-exchange membranes and electro-catalysts, and the study of mechanism of both the EOR and ORR in alkaline media [12–17]. Relatively, few investigations have been reported to the study of the fuel cell system. The core of the AEM DEFC
system is the membrane electrode assembly (MEA). The design of the MEA affects both the electrochemical active surface area (EASA) and the species transport behavior, and hence influencing the cell performance. Fig. 1a illustrates the state-of-the-art MEA structure for an AEM DEFC that is comprised of a pair of electrodes, including diffusion layer and catalyst layer, and an AEM held between the catalyst layers. This type of the anode electrode structure that has distinct catalyst and diffusion layers is directly borrowed from acid DAFCs, such as DMFCs [18–21]. In acid DMFCs, the separated and dense catalyst layer fabricated by mixing the high-conductivity cation ionomer (typically NaFon) and catalyst particles not only facilitates the proton transport resulting in reducing the cell resistance but also suppresses the methanol crossover so as to lower the cathode mixed potential, and thus improving the cell performance. In alkaline DEFCs, however, this type of MEA yields a low cell performance due to the low ion conductivity of both AEMs (typically A201) and anion ionomers (typically A3) [12]. Presently, an effective approach to enhance the ionic conductivity of the membrane is to add an alkali (typically the KOH) to the fuel solution [21–24]. This fuel-electrolyte-fed AEM DEFC yields a much higher cell performance, mainly because the increased pH value not only enhances the conductivity of the AEM but also improves the kinetics of the EOR [19]. However, an issue that has so far not been addressed in the cell system is whether the conventional anode electrode structure shown in Fig. 1a is the best design for the fuel-electrolyte-fed AEM DEFC. Being motivated by this issue, in this work, we propose a new anode electrode structure for the fuel-electrolyte-fed AEM DEFC. As shown in Fig. 1b, the electrode is composed of a nickel foam layer with thin catalyst films coated onto the skeleton of the foam having a smooth electron pathway and a three-dimensional cross-linked grid structure [25]. This design of the electrode enables the integration of the catalyst and diffusion layers, thereby extending the EASA and facilitating the mass and charge transport so as to significantly improve the cell performance.

2. Experimental

2.1. Preparation of membrane electrode assemblies (MEA)

An in-house fabricated AEM DEFC is composed of a MEA with an active area of 1.0 cm × 1.0 cm, sandwiched between a pair of current collectors, which were fixed by two fixture plates. The MEA consisted of a commercial cathode electrode with the Fe–Co HYPERMEC™ K14 catalysts (Acta), an anion-exchange membrane (A201, Tokuyama), and an in-house fabricated anode electrode. On the anode, catalyst inks were prepared by mixing the home-made PdNi/C [26] catalysts (average particle size: 3.5 nm) with a required loading and polytetrafluoroethylene (PTFE) with ethanol as the solvent. The content of the PTFE as a binder was maintained at about 5 wt.%. The catalyst inks were stirred continuously in an ultrasonic bath for 10 min such that they were well dispersed. Subsequently, two types of anode electrode fabricating method were used. The catalyzed-diffusion-media (CDM) method: the prepared catalyst inks were directly brushed onto the surface of the nickel foam (50 PPI, 1.0 mm in thickness) that served as the backing layer to form an anode electrode. The dip-coating (DC) method: the as-prepared catalyst inks was further diluted with the ethanol solvent and stirred continuously in an ultrasonic bath. The tailored nickel foam was first dipped in the catalyst inks for 1 min, and then withdrawn, subsequently, dried with a blower in the air, by which the catalysts with the binder were coated onto the skeleton of the nickel foam. Repeating the above-mentioned dip-withdraw-dry process until the required loading was coated onto the nickel foam to obtain the integrated anode electrode. It should be noted that, as compared with the spontaneous deposition, the electrodeposition and the thermal decomposition methods resulting in a large particle size (typically tens of nanometers) [3,25,27], the present dip-coating method that uses the PTFE as a binder to bind the as-prepared small catalyst particles (average particle size: 3.5 nm) onto the skeleton of the nickel foam results in a higher catalytic activity of the catalysts. In addition, the thin catalyst film on one surface of the integrated anode electrode was removed to reduce the contact resistance between the electrode and the current collector. Both the anode and cathode fixture plates were made of stainless-steel plates. A single serpentine flow field, having 1.0 mm channel width, 0.5 mm channel depth, and 1.0 mm rib width, was machined on one side of each fixture plate.

2.2. Measurement instrumentation and test conditions

The experiments were carried out in the cell test station detailed elsewhere [21]. Briefly, the voltage–current curves were controlled and measured by an electric load system (Arbin BT2000, Arbin Instrument Inc.). The aqueous solution, containing 3.0 M ethanol and 5.0 M KOH, was supplied to anode by a peristaltic pump at a flow rate of 1.0 ml min⁻¹. 99.5% oxygen without humidification at ambient pressure with a flow rate of 100 standard cubic centimeters per minute (scm) was fed to cathode by a mass flow controller (Omega FMA-78P4 and FMA-765A). The cell resistance was measured...
by the d.c.-pulse method. The surface morphology of the anode electrode was examined by a scanning electron microscope (JEOL-6390).

2.3. Measurement of EASA for the anode electrode by cyclic voltammetry

Cyclic voltammetry (CV) experiments were conducted to study the EASA of the anode electrode by using a three-electrode electrochemical cell assembly with a Pt foil and a Hg–HgO electrode (MMO, 1.0 M KOH) as the counter and reference electrodes, respectively. The as-prepared anode electrode having an active area of 1.0 cm × 1.0 cm was used as the working electrode. CV tests were then conducted at 50 mV s⁻¹ in the potential range between −0.926 and 0.274 V vs. MMO in 1.0 M KOH solution. Solutions were prepared from analytical grade reagents and deionized water.

3. Results and discussion

3.1. Cell performance comparison

Fig. 2 compares the cell performance of the AEM DEFC between two different MEAs, which consisted of the same cathode electrode, the same AEM but different anode

![Fig. 2 – Performance comparison of AEM DEFCs with different anode electrode structures.](image)

![Fig. 3 – CV curves of the different anode electrodes in 1.0 M KOH at a scan rate of 50 mV s⁻¹.](image)
electrode structures: the conventional separated anode electrode (represented by the square symbols) and the new integrated anode electrode (represented by the circle symbols). It is seen from the figure that the integrated anode yields a much better performance than the conventional design does: the peak power density of the integrated anode is 74 mW cm$^{-2}$, which is 37% higher than that of the conventional anode. It is also seen that the integrated anode yields a maximum current density of 580 mA cm$^{-2}$, which is 21% higher than the conventional design. The improved performance with the integrated anode can mainly be attributed to i) the increased EASA, ii) the enhanced mass transport, and iii) the reduced cell resistance.

i) The increased EASA: Fig. 3 shows the CV curves of both the integrated anode and the conventional anode with the same Pd loading. It can be seen that the peak area of the reduction of the palladium oxide ranging from −0.6 to 0 V in the integrated anode is significantly larger than that in the conventional anode, suggesting that the integrated anode yields a larger EASA. The larger EASA resulting from the integrated anode can be attributed to the fact that the catalyst can be well dispersed onto the skeleton of the nickel foam in the form of films, as evidenced from Fig. 4a and b. In contrast, being formed by brushing the catalyst ink onto the surface of the nickel foam, the catalyst layer of the conventional anode is much thicker and denser, as shown in Fig. 4c and d. In particular, large agglomerates may be formed in the catalyst layer of the conventional anode, inside which many catalyst particles are virtually inactive for the electrochemical reaction due to the coverage of the outer catalyst particles and binders. Hence, the integrated anode electrode yields a larger EASA.

ii) The enhanced mass transport: As evidenced from Fig. 2, the integrated anode can yield a higher maximum current density.
than the conventional anode, which means that the mass transport resistance in the integrated anode electrode is lower than that in the conventional anode electrode. This behavior can be explained as follows. With regard to the conventional anode electrode, the low porosity and small pore size are formed in the dense catalyst layer, which can be confirmed from the surface morphologies of the anode electrode shown in Fig. 4c. The low porosity and pore size result in a low permeability, resisting the mass transport of reactants and products. On the other hand, as illustrated in Fig. 4a, the integrated anode electrode made of nickel foam has a higher porosity and larger open pores, resulting in a higher permeability that facilitates the species transport. Hence, the mass transport is enhanced in the integrated anode electrode.

iii) The reduced cell resistance: Table 1 shows that the cell resistance of the conventional anode-based AEM DEFC is 346 mΩ cm², which is 23% higher than that of the integrated anode-based AEM DEFC. The lower cell resistance of the integrated anode-based AEM DEFC can in part be attributed to the fact that the higher permeability in the anode facilitates the transport of hydroxyl ions. A previous study showed [19] that the addition of the KOH to the fuel solution enhanced the conductivity of the hydroxyl ions in both the alkaline membrane and electrodes. Hence, the transport-enhanced integrated anode lowers the cell resistance. In addition, the electrons resulting from the EOR in the thin catalyst film can be quickly conducted to the current collector through the nickel foam that provides a continuous electron pathway shown in Fig. 4e and f, and hence further reducing the cell resistance. Therefore, the cell resistance is reduced in the integrated anode-based AEM DEFC.

3.2. Effect of the Pd loading

Fig. 5 shows the effect of the Pd loading in the integrated anode electrode on the cell performance. It can be seen that when increasing the Pd loading from 1.5 to 2.0 mg cm⁻², the cell performance is significantly increased. For instance, the peak power density increases from 66 to 102 mW cm⁻² as the Pd loading increases from 1.5 to 2.0 mg cm⁻². The increase in the peak power density is attributed to the increase in the EASA of the thin catalyst film coated on the skeleton of the nickel foam as a result of an increase in the Pd loading. However, it is found that a further increase in the Pd loading from 2.5 to 3.0 mg cm⁻² leads to a decrease in the cell performance. For instance, the peak power density decreases to 85 and 74 mW cm⁻², when the Pd loading is increased to 2.5 and 3.0 mg cm⁻², respectively. The best cell performance is achieved with the Pd loading of 2.0 mg cm⁻². The reason why a high Pd loading results in a low cell performance is attributed to the fact coating too much Pd onto the skeleton of the nickel foam will reduce open pores of the nickel foam, which not only reduces the EASA of thin catalyst films but also increases the mass and charge transport resistances. As a result, there exists an optimal Pd loading in the integrated anode for the best cell performance.

3.3. Effect of the operating temperature

Fig. 6 shows the effect of the operating temperature on the cell performance with the integrated anode electrode from 50 to 80 °C. It can be seen that the cell performance improves with an increase in temperature over the whole current density
region. The peak power density is 87 mW cm\(^{-2}\) at 50 °C, and it increases to 130 mW cm\(^{-2}\) at 80 °C. In addition, the maximum current density is 820 mA cm\(^{-2}\) at 50 °C, and it increases to 1060 mA cm\(^{-2}\) at 80 °C. The increase in the cell performance as a result of increasing the operating temperature can be explained as follows. On one hand, increasing the operating temperature increases the electrochemical kinetics of both the EOR at the anode and the ORR at the cathode, accordingly, increasing the cell voltage. On the other hand, the increase in the operating temperature enhances the mass and charge transports, which consequently reduces the ohmic loss and concentration loss. Therefore, the cell performance improves as the temperature is increased over the whole current density region, including the activation, ohmic and concentration-controlled regions.

4. Conclusions

Conventionally, the anode electrode structure that has distinct catalyst and diffusion layers has been used for both PEM and AEM DAFCs. In this work, we proposed a different anode electrode structure that integrates the diffusion and catalyst layers for fuel-electrolyte-fed AEM DEFCs. The integrated anode is composed of a nickel foam layer with thin catalyst films coated onto its skeleton. The experimental results indicate that the use of the integrated anode in the fuel-electrolyte-fed AEM DEFC can significantly improve the cell performance as compared with the use of the conventional anode that has separated catalyst and diffusion layers. The improved performance with the integrated anode can mainly be attributed to three reasons: i) the catalyst can be well dispersed onto the skeleton of the nickel foam in the form of films, resulting in a larger EASA; ii) relatively regular and large pore structures in the integrated anode facilitate the transport of reactants/products and ion charges; and iii) the integrated anode results in a reduced cell resistance. It is found that the nickel foam-based integrated anode electrode with the Pd loading of 2.0 mg cm\(^{-2}\) shows the best cell performance. It is also found that the AEM DEFC can yield a peak power density of 130 mW cm\(^{-2}\) and the maximum current density of 1060 mA cm\(^{-2}\) at 80 °C. The significance of the present work lies in the fact that an anode structure that combines diffusion and catalyst layers is more suitable for membrane-based fuel cells with diluted electrolyte solutions than the conventional design with distinct diffusion and catalyst layers.

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REFERENCES


