Agar chemical hydrogel electrode binder for fuel-electrolyte-fed fuel cells

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HIGHLIGHTS

- A novel ACH binder is synthesized for fuel-electrolyte-fed fuel cells.
- The ACH-based electrode offers better performance than the Nafion-based one does.
- A peak power density of 380 mW cm⁻² is achieved with the ACH-based electrode.
- The ACH binder can replace the Nafion ionomers in fuel-electrolyte-fed fuel cells.

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ABSTRACT

This work reports on the synthesis and application of a novel, cost-effective and environmentally friendly agar chemical hydrogel (ACHI) electrode binder in fuel-electrolyte-fed fuel cells. The ACH is synthesized by a chemical cross-linking reaction between agar and glutaraldehyde with acetic acid as a catalyst. The fuel cell performance characterization demonstrates that the use of the ACH-based electrode in a fuel-electrolyte-fed fuel cell enables an improvement in cell performance as opposed to the use of conventional Nafion ionomer-based electrodes. The improved performance can be mainly attributed to the enhanced mass/charge transport rendered by the hydrophilic nature and water retention characteristic of agar. This work suggests that the cost-effective ACH binder can replace conventional Nafion ionomers for fuel-electrolyte-fed fuel cells.

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1. Introduction

In preparing low-temperature solid-electrolyte fuel cell electrodes, an ionomer is essential not only to bind discrete catalyst particles to form a porous catalyst layer (CL), but also to provide the pathways for ions transporting from/to triple phase boundaries (TPB) [1]. In principle, anion-conducting ionomers (e.g.: A3) are used to conduct anions in anion exchange membrane fuel cells (AEMFCs) [2], whereas cation-conducting ionomers (e.g.: Nafion) are to conduct cations in proton exchange membrane fuel cells (PEMFCs) [3]. However, in fuel-electrolyte-fed fuel cell electrodes saturated with a liquid electrolyte (e.g.: NaOH/KOH, H₂SO₄) [4,5], ions conduct mainly through the liquid electrolyte, rather than through the solid electrolyte due to the fact that the ionic mobility in the liquid electrolyte is much higher than that in the solid electrolyte [6]. For this reason, an ionomer (solid electrolyte) used in a fuel-electrolyte-fed fuel cell system functions as a binder only, while the pathways for ion transport are mainly provided by the liquid electrolyte. Nevertheless, in the initial development stage of fuel-electrolyte-fed fuel cells, ionomers were generally employed as a result of the design concept of electrodes borrowed directly from solid-electrolyte fuel cells [7,8]. As shown in Fig. 1a, as Nafion is permeable to reactants (the dissolved phase [9]), the reactants can transport through the Nafion ionomer on the catalyst particles and reach the TPBs for the electrochemical reactions. Recently, attention has been paid to neutral binders for fuel-electrolyte-fed fuel cells [10–13]. Polytetrafluoroethylene (PTFE), a typical neutral binder, was added into the CL to serve as an electrode binder in past investigations [10]. However, as PTFE is impermeable to reactants, the reactants cannot penetrate the PTFE binder on catalyst particles, thereby reducing the effective active sites for electrochemical reactions, as shown in Fig. 1b. For this reason, more attention has been recently paid to the intrinsically hydrophilic neutral polymers [14,15]. Among the polymers used, hydrogels, three-dimensional solid polymeric networks that absorb and retain water in their polymeric matrices, are one of the most promising electrode binders for fuel-electrolyte-fed fuel cells [12,13]. Their unique characteristics of water absorption and retention are beneficial for reactants (the hydrogel phase) transport through the hydrogel binder on the catalyst particles and reaching the active
sites, as shown in Fig. 1c. As transporting reactants in hydrogels (the hydrogel phase) is similar to that in an aqueous solution (the liquid phase) [15], the transfer rate of reactants in the hydrogel phase is much higher than that in the dissolved phase (e.g.: Nafion). However, a barrier that limits the direct application of hydrogels in a fuel cell system is that the material is soluble in an aqueous solution [11]. Hence, water-insoluble hydrogels are needed, which can be formed by a cross-linking reagent [16]. Recently, Choudhury et al. [11] prepared a novel binder, chitosan chemical hydrogel (CCH), for a fuel-electrolyte-fed direct borohydride fuel cell (DBFC). The experimental results showed that the use of the CCH-based electrode yielded a peak power density of 81 mW cm$^{-2}$ [11]. The same group also reported on an electrode binder consisting of polyvinyl alcohol (PVA) chemical hydrogel (PCH) and demonstrated that the PCH-based DBFC could yield performance similar to the CCH-based DBFC [12].

Recently, we proposed a fuel-electrolyte-fed direct ethanol fuel cell (DEFC) consisting of an alkaline anode, a cation exchange membrane (CEM), and an acid cathode, termed as alkaline–acid DEFC (AA-DEFC) [17], as shown in Fig. 2. In this fuel cell system, as a CEM was employed (Na$^+$ ions as the charge carrier), a cation-conducting ionomer (Nafion) was used for preparing the electrodes [18]. In this work, we synthesized agar chemical hydrogel (ACH) by a chemical cross-linking reaction between agar and glutaraldehyde (GA) with acetic acid as a catalyst. The fuel cell performance tests at 60 °C demonstrated that the use of the ACH-based electrode yielded a higher peak power density (170 mW cm$^{-2}$) as compared to the Nafion-based electrode (150 mW cm$^{-2}$). More impressively, the use of the ACH-based electrode exhibited a peak power density of as high as 380 mW cm$^{-2}$ at 90 °C, which is even higher than the Nafion-based electrode (350 mW cm$^{-2}$).

2. Experimental

2.1. Preparation of the ACH-based electrode

A simple cross-linking reaction described elsewhere [19,20] was used in preparing the ACH-based electrode. Briefly, the steps are as follows: (1) 38 mg agar was completely dissolved in 20 mL deionized (DI) water at 90 °C; (2) 5 wt.% GA solution was gradually added into the agar aqueous solution and stirred for 10 min; (3) 30 wt.% Au/C catalyst was added into the agar–GA mixed solution with a 10-min magnetic stirring; (4) the slurry was passed on a piece of carbon cloth; (5) the prepared electrode was immersed in 1.0 M acetic acid solution for 12 h to cause the cross-linking reaction between agar and GA; and (6) the prepared electrode was washed with the DI water and the accurate Au loading was weighed (catalyst loading: 1.2 mg cm$^{-2}$, ACH content: 10 wt.%) after drying at room temperature.

2.2. Preparation of agar polymers for FT-IR analysis

Two polymers (A and B) were synthesized for the FT-IR analysis. Polymer A (agar polymer with the cross-linking treatment): the experiment process underwent the first two steps in Section 2.1. After that, the agar–GA mixed solution was cast into a membrane in a Petri dish. Then, the cast membrane was directly immersed in 1.0 M acetic acid solution for the cross-linking reaction. Polymer B (agar polymer without the cross-linking treatment): the experiment process only underwent the first step in Section 2.1 and then the agar aqueous solution was cast into a membrane. Finally, both polymers were washed by the DI water and then dried at room temperature.

![Fig. 1. Schematic of reactants transport through the respective polymer on the catalyst particles: (a) Nafion; (b) PTFE and (c) Hydrogel.](image)

![Fig. 2. Schematic of an alkaline–acid direct ethanol fuel cell (AA-DEFC).](image)
2.3. MEA fabrication and measurement instrumentation

Each membrane electrode assembly (MEA) consisted of an in-house fabricated anode, a CEM (Nafion 117), and an in-house fabricated cathode. The pre-treatment of the Nafion membrane can be found elsewhere [21]. The anode CL was made of PdNi/C (1.0 mg cm$^{-2}$) and Nafion ionomer (5 wt.%), and the anode backing layer (BL) was the nickel foam. For comparison, a conventional cathode electrode was fabricated. The CL was made of Au/C (1.2 mg cm$^{-2}$) and Nafion ionomer (10 wt.%), and the BL was carbon cloth. More detailed information about the MEA fabrication can be found elsewhere [4,5]. The prepared MEAs were sandwiched between a pair of current collectors. Cell performances were measured by using an electric load system (Arbin BT2000).

3. Results and discussion

3.1. Agar chemical hydrogel

Agar is a biodegradable, hydrophilic, cheap, non-toxic, and chemically stable natural polymer. Agar hydrogel can be easily formed by heating agar in DI water and subsequently cooling the agar solution in air, which has been widely applied in the medical, agricultural, drug packaging and release, cosmetics and food industries [22]. As agar hydrogel can be dissolved in hot water (85–90 °C) [23], it cannot be directly used as the electrode binder in fuel-electrolyte-fed fuel cells. An effective approach is to form the water-insoluble ACH binder by a chemical cross-linking reaction [24], as shown in Fig. 3. Unlike the Nafion ionomer, as the hydrogel can absorb a larger amount of water, a unique 3-D structure is created after water absorption and retention, facilitating the mass/charge transport [13,16]. Therefore, the ACH-based electrode possesses a lower mass/charge transport resistance than the Nafion-based electrode does.

3.2. FT-IR analysis

The FT-IR analysis was conducted to confirm whether the cross-linking reaction takes place when the agar–GA mixed solution meets the acetic acid. Fig. 4 presents the FT-IR spectra of the agar polymer with the cross-linking treatment (Polymer A) and the agar polymer without the cross-linking treatment (Polymer B). It can be seen that the FT-IR spectra of two agar polymers show an absorption band at about 3400 cm$^{-1}$, which is ascribed to O–H stretching, while the peak at 2900 cm$^{-1}$ is attributed to the methoxyl groups. As compared to the spectrum of Polymer B, A exhibits the characteristic band at about 1710 cm$^{-1}$ associated with the stretching of C=O groups, which appear after the cross-linking treatment [25]. This result proves that the cross-linking reaction took place, and thus the ACH was successfully synthesized.

3.3. SEM images

Fig. 5 shows the surface morphologies of the Nafion-based electrode and the ACH-based electrode. It can be seen that the Nafion-based electrode shows a dense CL on the substrate (carbon cloth), suggesting that the mass/charge transport resistance is relatively large [26]. On the other hand, the ACH-based electrode shows a polymer-like surface, indicating that the ACH-based electrode can deliver the reactants to the active sites at a high rate due to its high capabilities of water absorption and retention [15].

3.4. Cell performance

Fig. 6 compares the cell performance of the AA-DEFC with two different MEAs consisting of the same anode, the same CEM, but different cathode electrodes. It can be seen from Fig. 6a that the cell with the ACH-based electrode yields a peak power density of 170 mW cm$^{-2}$ at 60 °C, which is even higher than that with the Nafion-based cathode (150 mW cm$^{-2}$). Also, the use of the ACH-based electrode enables the cell yield a maximum current density of 470 mA cm$^{-2}$, which is also higher than the Nafion-based...
As mentioned earlier, the reactants transport through the Nafion ionomers in the form of the dissolved phase and then reach the TPBs for electrochemical reactions. On the other hand, the reactants transport through the hydrogels in a fashion similar to an aqueous solution, enhancing the mass/charge transport to the reaction sites. Hence, the improved performance is mainly attributed to the enhanced mass/charge transport rendered by the hydrophilic nature and water retention characteristic of agar. It is seen from Fig. 6b that when the operating temperature increased to 90 °C, the performance was dramatically boosted as a result of the improved electrochemical kinetics, the increased ionic conductivity of the membrane, and the enhanced mass/charge transport. Specifically, the cell with the ACH-based electrode yields a higher peak power density (380 mW cm⁻²) as compared to the Nafion-based electrode (350 mW cm⁻²). In addition, the use of the ACH-based electrode exhibits a higher maximum current density (1000 mA cm⁻²) as opposed to the Nafion-based electrode (950 mA cm⁻²). This result further confirms that the mass/charge transport resistance through the Nafion ionomer (the dissolved phase) is still larger than that through the ACH binder (the hydrogel phase) at 90 °C. To confirm the stability of the ACH-based electrode, the constant-current discharging was conducted and is presented in Fig. 7. It is shown that no degradation in the cell voltage was found during the 10-h continuous operation, suggesting the good stability of the ACH-based electrode.

In summary, the experimental results demonstrated that this novel, cost-effective, and environmentally friendly ACH binder
can successfully replace the ionomers (e.g.: Nafion) in fuel-electrolyte-fed fuel cells.

4. Concluding remarks

We have synthesized a novel, cost-effective and environmentally friendly ACH electrode binder for fuel-electrolyte-fed AA-DEFCs by a chemical cross-linking reaction between agar and GA with acetic acid as a catalyst. We tested the ACH binder in a fuel-electrolyte-fed AA-DEFC and showed that the ACH-based electrode enabled an improvement in cell performance as opposed to the use of conventional Nafion-based electrodes. The improved performance is mainly attributed to the enhanced mass/charge transport rendered by the hydrophilic nature and water retention characteristic of agar. More impressively, a peak power density of as high as 380 mW cm$^{-2}$ is achieved with the ACH-based electrode at 90 °C, which represents the highest performance of DEFCs that has so far been reported in the open literature. In addition, the transient discharging behavior demonstrated that the ACH-based electrode possesses a good stability. The significance of the present work lies in the fact that the cost-effective ACH binder can replace conventional Nafion ionomers in fuel-electrolyte-fed AA-DEFCs.

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