Carbon-neutral sustainable energy technology: Direct ethanol fuel cells

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A B S T R A C T

Ethanol is a sustainable, carbon-neutral transportation fuel. It is an ideal fuel source for direct oxidation fuel cells for portable and mobile applications, as it offers multiple advantages over hydrogen and methanol, including ease of transportation, storage and handling as well as higher energy density. Tremendous efforts have been made to improve direct ethanol fuel cells (DEFC) that use proton exchange membranes. This type of acid DEFC still exhibits low performance (the state-of-the-art peak power density is 96 mW cm$^{-2}$ at 90°C), despite employing expensive platinum-based catalysts. However, it has been recently demonstrated that the use of anion exchange membranes and non-platinum catalysts in DEFCs enables a dramatic boost in performance (the state-of-the-art peak power density can be as high as 185 mW cm$^{-2}$ at 60°C). This article provides an overview of both acid and alkaline DEFC technologies by describing their working principles, cell performance, system efficiency, products of the ethanol oxidation reaction, and cost. Recent innovations and future perspectives of alkaline DEFCs are particularly emphasized.

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1. Introduction

The growing global energy demand and the large-scale use of CO₂-emitting fossil fuels have created a tremendous strain on the planet’s natural resources. Hence, developing renewable energy sources at a global scale is critical for sustainable growth, especially in developing countries [1]. Fuel cells directly convert chemical energy stored in fuels into electrical energy through electrochemical reactions, and have been identified as one of the most promising technologies for the clean energy industry of the future [2]. Hydrogen is a commonly used fuel to energize fuel cells, particularly proton exchange membrane fuel cells (PEMFC) [3]. However, the production of pure hydrogen is cost-inefficient, and there are many challenging issues in transporting, storing, and handling hydrogen. For these reasons, liquid fuels, which exhibit much higher energy density and are easier to transport, store, and handle, have become an attractive alternative to hydrogen for fuel cells [4–6]. Among various fuels, methanol has been considered the most promising primarily because it is the simplest alcohol and making it easier to oxidize than other alcohol fuels. Hence, direct methanol fuel cells (DMFC) have been extensively investigated over the past few decades [7,8]. However, DMFC technology faces technical issues associated with sluggish anode reaction kinetics [9] and methanol crossover [10]. Furthermore, the inherent disadvantage of methanol is its toxicity and volatility, which does not translate well for large-scale consumer use [11]. In contrast, ethanol is much less toxic than methanol; it has higher specific energy (8.0 kWh kg⁻¹) than methanol (6.1 kWh kg⁻¹) and can be produced in great quantities from biomass or even agricultural waste. More importantly, the CO₂ emitted during the energy production process from ethanol can be soaked up by growing plants from which the fuel is produced [12]. Ethanol is, therefore, a sustainable, carbon-neutral fuel source. Generally, DEFCs can be divided into two categories in terms of the employed electrolyte, i.e., acid DEFC and alkaline DEFC. This article provides a brief analysis of the development of two types of DEFC from the point of view of the system.

2. Acid DEFC

Fig. 1a shows a typical acid DEFC that consists of a membrane electrode assembly (MEA), sandwiched by an anode and a cathode bipolar plate. The MEA, a multi-layered structure, is sequentially composed of an anode diffusion layer (DL), an anode catalyst layer (CL), a proton exchange membrane (PEM), a cathode CL, and a cathode DL. The PEM (typically Nafion) as the core component is to functionally conduct protons from the anode to the cathode, and physically act as a separator between the anode and the cathode. The CLs are normally comprised of a mixture of catalysts (typically PtSn for the ethanol oxidation reaction (EOR) and Pt for oxygen reduction reaction (ORR)) and ionomers (typically Nafion) to provide triple phase boundaries (TPB) for the electrochemical reactions. The DLs consist of two layers, a backing layer (BL) made of carbon cloth or carbon paper, and a micro-porous layer (MPL), usually composed of a mixture of hydrophobic polymer (typically PTFE) and carbon powder. The following subsections will introduce the working principle, cell performance, products of the EOR, system efficiency, as well as system cost.

2.1. Working principle

On the anode, ethanol solution is supplied through the anode flow field to the anode CL, where ethanol is oxidized to theoretically generate electrons, protons, and carbon dioxide:

CH₃CH₂OH + 3H₂O → 2CO₂ + 12H⁺ + 12e⁻,  \( E_o^i = 0.09 \) V  \( (1) \)

On the cathode, oxygen/air is supplied through the cathode flow field and transfers through the cathode DL to the cathode CL, where oxygen reacts with the protons that are conducted through the PEM from the anode and the electrons that come from the external circuit to form water according to

O₂ + 4H⁺ + 4e⁻ → 2H₂O,  \( E_o^i = 1.23 \) V  \( (2) \)

Combining the EOR given by Eq. (1) and the ORR given by Eq. (2) results in an overall reaction for acid DEFCs:

CH₃CH₂OH + 3O₂ → 2CO₂ + 3H₂O,  \( E_o^o = 1.14 \) V  \( (3) \)

However, it should be noted that with the state-of-the-art catalysts, the complete oxidation of ethanol expressed by Eq. (1) is not achieved. It is generally agreed that the main products of the EOR are acetaldehyde and acetic acid with a mole ratio of around 1:1 [13]:

CH₃CH₂OH + 1/2H₂O → 1/2CH₃COOH + 1/2CH₃CHO + 3H⁺ + 3e⁻  \( (4) \)

Hence, the actual overall reaction in acid DEFCs with the state-of-the-art catalysts is

CH₃CH₂OH + 3/4O₂ → 1/2CH₃COOH + 1/2CH₃CHO + H₂O  \( (5) \)

2.2. Performance

The striking feature of acid DEFCs is that the entire system setup, including all components, is borrowed from PEMFCs. Although tremendous efforts have been made on developing catalysts toward the EOR for acid DEFCs, the cell performance remains low, even at high operating temperatures (e.g. 96 mW cm⁻² at 90 °C), as listed in Table 1. The low performance of acid DEFCs can be mainly attributed to the sluggish kinetics of the EOR in acid media, thereby leading to a
large activation loss [45]. For this reason, the development of acid DEFCs is presently focused on the synthesis of highly active catalysts toward the EOR [46].

### 2.3. Products of the EOR

The electro-oxidation of ethanol is believed to be a complex multi-step reaction through both the C1-pathway (oxidizing CH3CH2OH to CO2) and C2-pathway (oxidizing CH3CH2OH to CH3COOH/CH3CHO) [47]. Unlike the complete oxidation of ethanol to CO2 that yields 12 electrons per ethanol molecule, the incomplete oxidation of ethanol to acetaldehyde and acetic acid liberates only 2 and 4 electrons, respectively. In acid DEFCs, the products of the EOR have proven to be a mixture of acetaldehyde, acetic acid and CO2 [48–50]. Among those products, the amount of CO2 produced by the EOR in acid media is small (< 5%) [49]. Hence, it is generally agreed that the main products of the EOR in acid media are currently acetaldehyde and acetic acid with a molar ratio of around 1:1 [12], as shown in Eq. (4). It should be noted that acetic acid is nontoxic, highly soluble in water and less corrosive on soil so that it has been widely used as the important chemical reagent and industrial chemical. For example, it is used to produce polyethylene terephthalate, cellulose acetate, polyvinyl acetate, and synthetic fibers, and is also used as a food additive for an acidity regulator and a condiment [51,52]. Hence, acetic acid can be readily accepted as the final product of the EOR. However, the other main product, acetaldehyde, is undesirable. The electro-oxidation of ethanol to acetaldehyde only releases 2 electrons per ethanol molecule, resulting in an 83.3% loss in the Faradic efficiency [53]. In addition, acetaldehyde is toxic when applied externally for prolonged periods, is an irritant and a probable carcinogen [54]. Therefore, achieving the direct 12-electron oxidation of ethanol is a critical issue to overcome.

### 2.4. System efficiency

Aside from the performance, another criterion to evaluate a fuel cell system is the energy-conversion efficiency determined by the following three specific efficiencies [55]:

i) Thermodynamic efficiency ($\eta_t$) is the theoretical energy-conversion efficiency, meaning that the change in the Gibbs free energy of an overall reaction, $\Delta G_f$, is completely converted into electricity:

$$\eta_t = \frac{\Delta G_f}{\Delta H_f}$$

where $\Delta H_f$ denotes the enthalpy change of an overall reaction. Under standard conditions (1.0 atm and 298.15 K), $\Delta G_f = -1325 \text{ kJ mol}^{-1}$ and $\Delta H_f = -1367 \text{ kJ mol}^{-1}$ [48]. Hence, the thermodynamic efficiency of acid DEFCs is 97%.

ii) Voltage efficiency ($\eta_{Ecell}$) is caused by the electrode overpotentials and defined as

$$\eta_{Ecell} = \frac{E_{cell}}{E}$$

where $E_{cell}$ denotes the operating voltage (typically 0.5 V), and $E$ is the reversible cell voltage (1.14 V). Hence, the voltage efficiency of acid DEFCs is 44%.

iii) Faradic efficiency ($\eta_f$) is caused by the incomplete oxidation of ethanol and defined as

$$\eta_f = \frac{n_e}{n_i}$$

where $n_e$ represents the actual number of the electrons released from the EOR and $n_i$ denotes the theoretical number of the electrons released from the EOR. Due to the fact that the main products of the EOR in acid media are acetaldehyde and...
efficient catalysts and PEMs is the critical issue in the process of manufacturing acid DEFCs.

3. Alkaline DEFC

It has been recently demonstrated that when the acid electrolyte is switched to an alkaline one, i.e., anion exchange membrane (AEM), the cell performance improves substantially, mainly due to faster kinetics of both the EOR and ORR in alkaline media, even with the use of non-precious metal catalysts (the state-of-the-art peak power density can be as high as 185 mW cm\(^{-2}\) at 60 °C). Additionally, it can be seen from Fig. 1 that, unlike dragging ethanol and water molecules from the anode to the cathode in acid media, the charge carriers (OH\(^{-}\)) in alkaline media drag both molecules back to the anode, alleviating the ethanol and water crossovers [57]. For these reasons, alkaline DEFCs have recently attracted increasing attention [58–65]. Fig. 1b illustrates the typical structure of an alkaline DEFC composed of an anode and a cathode separated by an AEM, which is borrowed from the acid DEFC. It should be noted that the AEM (typically A201 by Tokuyama) is to functionally conduct hydroxyl ions from the cathode to anode in addition to acting as a separator between the anode and cathode. Typically, quaternized hydrocarbon AEMs (e.g., A201 by Tokuyama) are used in alkaline DEFCs [59]. Similarly, two CLs are usually comprised of a mixture of catalysts and ionomers (e.g., A3) to form TPBs for the EOR and ORR. The catalysts typically for the EOR and ORR in alkaline media are Pd-based catalysts and FeCo catalysts, respectively [66]. It should be mentioned that in alkaline DEFCs, nickel foam is usually employed as the anode BL, facilitating the mass transport of aqueous molecules back to the anode, alleviating the ethanol and water crossovers [57]. For these reasons, alkaline DEFCs have recently attracted increasing attention [58–65].

3.1. Working principle

The fuel solution flowing into the anode flow field is transported through the anode DL to the anode CL, where ethanol is oxidized to theoretically generate electrons, water, and carbon dioxide [12]:

\[
\text{CH}_3\text{CH}_2\text{OH} + 12\text{OH}^{-} \rightarrow 2\text{CO}_2 + 9\text{H}_2\text{O} + 12\text{e}^{-}, \quad \text{E}^{\circ}_a = -0.74 \text{V} \quad (10)
\]

The water in fuel solution, along with water produced from the EOR, diffuses through the membrane to the cathode, while the electrons produced pass through an external electrical load to the cathode. On the cathode, the oxygen/air provided by the cathode flow field is transported through the cathode DL to the cathode CL, where oxygen combines with electrons and water from the anode to produce OH\(^{-}\) ions:

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^{-} \rightarrow 4\text{OH}^{-}, \quad \text{E}^{\circ}_c = 0.40 \text{V} \quad (11)
\]

Subsequently, the generated OH\(^{-}\) ions are conducted through the membrane to the anode for the EOR. Combining the EOR given by Eq. (10) and the ORR given by Eq. (11) results in an overall reaction for the alkaline DEFCs:

\[
\text{CH}_3\text{CH}_2\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}, \quad \text{E}^{\circ} = 1.14 \text{V} \quad (12)
\]

It should be noted that with the existing catalysts, the main product of the EOR in alkaline media is acetic acid (acetate), rather than carbon dioxide [68]:

\[
\text{CH}_3\text{CH}_2\text{OH} + 5\text{OH}^{-} \rightarrow \text{CH}_3\text{COO}^{-} + 4\text{e}^{-} + 4\text{H}_2\text{O} \quad (13)
\]
Hence, the actual overall reaction in alkaline DEFCs with the state-of-the-art catalysts is

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}
\]

(14)

3.2. Performance

The architectural design of an alkaline DEFC system is similar to that of acid DEFCs, in which the ion transport pathways between the anode and cathode are formed by the network of dispersed ionomers in the electrodes that are interfaced with the membrane. However, such a fuel cell system, which entirely relies on an AEM to conduct ions through the membrane and ionomers in the electrodes, exhibits extremely low cell performance (the state-of-the-art peak power density is 1.6 mW cm\(^{-2}\)) [69], primarily because of the low conductivity of the state-of-the-art AEMs and corresponding ionomers. Previous efforts, with respect to the development of alkaline DEFCs, therefore, have mainly been made to develop the high-conductivity ion-conducting materials [70]. It has recently been demonstrated that, even using existing ion conductors and catalysts, an addition of an alkali (e.g.: NaOH and KOH) to ethanol would enable alkaline DEFCs to yield substantially high performance (the state-of-the-art peak power density can be as high as 185 mW cm\(^{-2}\) at 60 °C) [88].

3.3. Products of the EOR

Product analysis of the EOR in alkaline media has been extensively investigated by using in-situ Fourier transform infrared (FTIR) spectroscopy combined with cyclic voltammetry [105,106] and NMR spectroscopy [80]. The analysis indicates that with the existing catalysts, the main product of the EOR in alkaline media is acetic acid (acetate). Unlike acid media, acetaldehyde is an active intermediate rather than the final product. Hence, the electro-oxidation of ethanol is believed to be predominated by the C\(_2\)-pathway (oxidizing CH\(_3\)CH\(_2\)OH to CH\(_3\)COOH/CH\(_3\)CHO). The electro-oxidation of ethanol to acetic acid (acetate) through a 4-electron pathway means that the loss of the Faradic efficiency of alkaline DEFCs is as high as 66.7%, as compared to the complete oxidation of ethanol to CO\(_2\) that releases 12 electrons [47]. Therefore, the complete electro-oxidation of ethanol to CO\(_2\) remains a challenging issue in alkaline DEFCs.

3.4. System efficiency

Thermodynamic efficiency (\(\eta_t\)) is calculated according to the overall reaction, as mentioned in Section 2.4. As two DEFCs have the same theoretical overall reaction, the thermodynamic efficiency of alkaline DEFCs is 97%. Similarly, the operating voltage is set to be 0.5 V so that voltage efficiency (\(\eta_v\)) of alkaline DEFCs is 44%. Presently, the literature reports that the main product of the EOR in alkaline media is acetic acid (acetate), and the CO\(_2\) current is attributed to the addition of base, which not only allows a dramatic increase in the ionic conductivity, but also enables the kinetics of the EOR to be speeded up further [103,104].
efficiency (CCE) varies from 6% to 30.6% [47]. As such, Faradic efficiency ($\eta_F$) of the state-of-the-art alkaline DEFCs is in the range from 37% to 54%. The actual energy–conversion efficiency of the alkaline DEFCs can be determined by multiplying three specific efficiencies. It indicates that with the existing catalysts, operating an alkaline DEFC at 0.5 V results in the total energy–conversion efficiency varying from 16% to 23%, which is still lower than that of acid DMFCs ($\eta_C=37\%$) [56], but about two times higher than that of DEFCs. It is clear that the main loss of the energy-conversion efficiency is attributed to the incomplete electro-oxidation of ethanol. If a direct 12-electron electro-oxidation of ethanol could be achieved, the total energy-conversion efficiency of two DEFCs would be as high as 43%, which is comparable with that of acid DMFCs. For this reason, many attempts have been made to synthesize the highly selective catalysts to improve the CO$_2$ selectivity of the EOR [107–109]. Shen et al. [107] synthesized the carbon supported Pt/Rh catalysts to improve the CO$_2$ selectivity in alkaline media, and suggested that the C–C bond cleavage was the preferred pathway for the dissociation of ethanol on Rh surface. However, there is still distance to cover from the direct 12-electron electro-oxidation of ethanol in a real fuel cell system. Future consideration of catalyst material should not only aim for high activity toward the EOR, but also high CO$_2$ selectivity of the EOR.

3.5. Cost

One competitive advantage of alkaline DEFCs is the cost-effectiveness of the materials. Fig. 2b shows the cost of alkaline DEFCs, which is calculated based on the experimental results in Ref. [89]. It can be seen that the cost of alkaline DEFCs is estimated to be 612 $/kW, which is much lower than that of acid DEFCs (3369 $/kW). The low cost per unit power is attributed not only to the use of non-platinum catalysts and alkaline electrolyte membranes (e.g., A201 by Tokuyama) in alkaline DEFCs as compared to the use of Pt-based catalysts and Nafion membranes in acid DEFCs [46,110,111], but also to the high power density of the state-of-the-art alkaline DEFCs (185 mW cm$^{-2}$). Therefore, low-cost alkaline DEFCs are more competitive commercially than the more expensive acid DEFCs.

4. Innovative system design

Aside from the above-mentioned factors, another important parameter that limits the performance of DEFCs operated under both acid and alkaline media is that thermodynamically, their theoretical voltage is low (1.14 V). Recently, An et al. [93] proposed a novel DEFC that consists of an alkaline anode, a membrane, and an acid cathode employing hydrogen peroxide as the oxidant, termed as alkaline-acid DEFC (AA-DEFC), as shown in Fig. 1c. It is worthwhile to note that when the oxidant is changed from oxygen to hydrogen peroxide, further to the acidified hydrogen peroxide, the theoretical voltage of DEFCs is eventually increased to 2.52 V [93]. Experimentally, it has been demonstrated that the AA-DEFC can yield a much higher peak power density of 360 mW cm$^{-2}$ at 60 °C [91], which represents the highest performance of DEFCs that has so far been reported in open literature. However, there are two critical issues in the new system, i.e., the species crossover and hydrogen peroxide decomposition [112]. Specifically, the species crossover will create a mixed potential and decrease the cell performance, while the hydrogen peroxide decomposition will cause a significant decrease in the cathode potential and thus dramatically decrease the cell performance [112]. To address the issue of the H$_2$O$_2$ decomposition, An et al. [94] proposed a bifunctional electrode architecture for the AA-DEFC and showed that the new electrode architecture not only alleviates the problem of H$_2$O$_2$ decomposition, but also enhances the mass transport of reactants/products [90]. It should be noted that while the theoretical voltage of this system is as high as 2.52 V, there is still plenty of room for the cell performance to be further improved. A unique feature associated with the use of hydrogen peroxide as oxidant in this system is its high volumetric power density, making this power pack particularly suitable for space or underwater applications where oxygen is not readily available. On the other hand, although the fuel cell system shows substantially higher performance than conventional DEFCs, some fundamental issues in this new type of fuel cell, such as the species crossover and hydrogen peroxide decomposition, need to be addressed in future studies.

5. Summary and perspective

Ethanol is a sustainable, carbon-neutral transportation fuel source. It is an ideal fuel source for direct oxidation fuel cells for portable and mobile applications because it offers multiple advantages over hydrogen and methanol, including higher energy density and ease of transportation, storage, and handling. However, acid DEFCs that use Pt-based catalysts and Nafion membranes exhibit low performance (96 mW cm$^{-2}$ at 90 °C). When the acid electrolyte was substituted with an alkaline electrolyte, the cell performance was improved substantially, even with non-platinum catalysts (185 mW cm$^{-2}$ at 60 °C). Aside from this exciting cell performance result, this type of DEFC offers two other competitive advantages, i.e., high efficiency and low cost. In fact, the stellar performance of alkaline DEFCs is mainly attributed to the addition of an alkali in fuel solution. Several problems must be addressed with this addition, namely (i) carbonate produced by the reaction between the permeated alkali and CO$_2$ from the air reduces the ionic conductivities of alkaline membranes and corresponding ionomers; (ii) the carbonate precipitation reduces the hydrophobicity of the porous electrode, thus breaking the balance of mass transport between water and oxygen; and (iii) alkaline membranes exhibit poor chemical stability in a strong alkaline environment. The aforementioned problems are introduced by the addition of a base, and a likely solution is to avoid the involvement of bases, i.e., developing base-free alkaline DEFCs that purely rely on the solid anion-conducting electrolyte (membrane and ionomer). The future direction of development should be focused on engineering high-conductivity anion-conducting materials, and high-activity, high-selectivity catalysts.

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References
