Scalable Membraneless Direct Liquid Fuel Cells Based on a Catalyst-Selective Strategy

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This perspective presents a membraneless direct liquid fuel cell (DLFC) concept based on a catalyst-selective strategy. The membraneless DLFCs are operated at low temperatures by employing a non-precious cathode catalyst with a high catalytic selectivity. The uniqueness is that the inexpensive cathode catalyst only catalyzes the oxygen reduction reaction but does not catalyze the oxidation reaction of a specific fuel. Therefore, during the operation of DLFCs, the liquid fuel can enter the cathode freely without any concern of fuel crossover. This catalyst-selective approach tactfully avoids the use of high-cost or technically unviable ion-exchange polymer membranes in DLFCs. The catalyst-selective operating principle also overcomes the scalability issue of the traditional laminar-flow membraneless DLFCs. Through a proper management of the anode and cathode catalysts in the cell, a variety of inexpensive, renewable alcohols, and small-molecule organics can be employed as anode fuels. This innovative approach of membraneless alkaline DLFCs offers a great opportunity for the development of inexpensive energy-generation systems for both mobile and stationary applications. In addition to summarizing the principle and the research progress of the unique membraneless DLFC platform, the challenges and future research directions are presented.

1. Introduction

The pressing need for a sustainable energy future is driving the advancement of fuel cell technologies.[1] Fuel cells are considered as one of the key energy technologies in the future for both transportation and household heating systems.[2] Among the various types of fuel cells, the low-temperature proton-exchange membrane (PEM)-based direct liquid fuel cells (DLFCs) have drawn considerably attraction as promising energy-generation systems for both portable and stationary applications.[3] In comparison with gaseous hydrogen fuel, liquid fuels have several significant advantages, as they can be easily stored, transported, and managed.[3] Also, liquid fuels have significantly higher mass-energy density than gaseous fuels.[4] However, the DLFC technologies are facing a series of "bottlenecks" limitations that hamper their commercialization.[5] It has generally been considered that the high cost of Nafion® membrane and the sluggish electrode reaction kinetics are two major obstacles associated with the low-temperature PEM-based DLFCs.[6]

At present, DLFCs are mostly developed with PEMs and are operated in a weakly acidic environment.[7] Under the acidic operating condition, carbon dioxide generated from anodic reactions can be easily removed from the DLFC system.[8] However, there are kinetic constraints with both the fuel oxidation reaction (FOR) and the oxygen reduction reaction (ORR) in acidic media, which is a major contribution to the relatively low performance of DLFCs.[9] To enhance the electrode reaction kinetics, operating DLFCs under an alkaline condition has been recognized as an effective approach.[10] The recent development of anion-exchange polymer membranes has reinvigorated the development of DLFCs with an OH^--conducting electrolyte membrane.[11] Quite a few DLFC systems have already been demonstrated with an alkaline anion-exchange polymer electrolyte membrane.[12] However, although there have been extensive research, the development of hydroxide-exchange polymer membranes is not yet practically viable to meet the demand of alkaline DLFC technologies.[13]

To avoid the use of anion- or cation-exchange membranes, operation of DLFCs by controlling laminar (without mixing) flows of the liquid fuel and oxygen (air) has been attempted.[14] The DLFCs can be operated without an ion-exchange membrane if the flow streams of the fuel and air are well manipulated based on the laminar flow of two streams in a microchannel.[15] There have been extensive research on the cell configuration design and improvement of the cell performance.[16] With careful considerations of the coupled mass transport and the electrochemical kinetics, high-performance membraneless DLFCs can be achieved.[17] However, this membraneless approach is theoretically based on the laminar-flow fluid mechanics, which limits the scalability of DLFC devices.[18] The laminar-flow membraneless fuel cells can only be fabricated to millimeter-scale sizes, limiting their practical applications.[19]

In view of the above issues, the DLFC technologies are currently in a very challenging situation. The major concerns are 1) high cost of catalysts due to the sluggish electrode reactions in the PEM-based DLFCs, 2) high cost of PEMs in PEM-based DLFCs, 3) a lack of reliable and viable hydroxide-exchange membranes for the development of alkaline DLFCs, and 4) scalability limitation of the laminar-flow membraneless DLFCs.

This perspective presents a recently proposed membraneless DLFC concept. The membraneless approach is enabled by a catalyst-selective strategy through employing an inexpensive cathode catalyst, which not only exhibits an expected activity for the ORR but also exhibits a

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desired inactivity for the oxidation reaction of a specific fuel. The catalyst-selective operating principle does not have a scalability limitation issue and is promising to break through all the currently existing "bottleneck" obstacles of the DLFC technologies. This perspective first introduces the principle and uniqueness of the "catalyst-selective strategy." Then, a few highly selective cathode catalysts are discussed in terms of their activity for ORR and their inactivity for FOR. Afterward, a number of membraneless DLFC systems developed with the "catalyst-selective strategy" as well as their performance are summarized. Finally, future efforts and directions are proposed.

2. Concept, Principle, and Uniqueness of the Catalyst-Selective Membraneless DLFCs

In the traditional DLFC, use of an ion-exchange membrane is required to prevent the oxidants and liquid fuel from mixing with each other. If a fuel enters the cathode, a FOR would occur as most cathode catalysts (e.g., the commonly used Pt) also catalyze the FOR.[20] The philosophy with the catalyst-selective strategy is schematically illustrated in **Figure 1**.[21] The central effort of this strategy is the use of a cathode catalyst, which provides a high ORR activity but does not catalyze the oxidation reaction of a specific fuel in alkaline media, as schematized in Figure 1a. Therefore, the operation of DLFCs would allow the anode fuel to freely enter the cathode without any fuel crossover concerns.[21,22] On the other hand, as a general scenario, the diffusivity and solubility of gaseous O_2 is fairly low in aqueous solutions.[23] Therefore, the oxygen crossover from the cathode to the anode is not an issue at all. Thus, the operation of DLFCs with a catalyst-selective cathode catalyst does not need an ion-exchange (hydroxide-ion) membrane in the cell, as illustrated in Figure 1b.

In the traditional membrane-based DLFCs, the ion-exchange membrane also plays an important role to provide an ion transport path to sustain the redox reactions at the anode and cathode.[24] For instance, cation-exchange membranes usually provide a proton transport path in PEM-based DLFCs, whereas anion-exchange membranes provide a hydroxide-ion transport path in alkaline DLFCs. The ionic path between the cathode and the anode in the catalyst-selective membraneless DLFCs is generally addressed by the addition of a supporting electrolyte to the anode fuel (Figure 1b). The supporting electrolyte should be able to
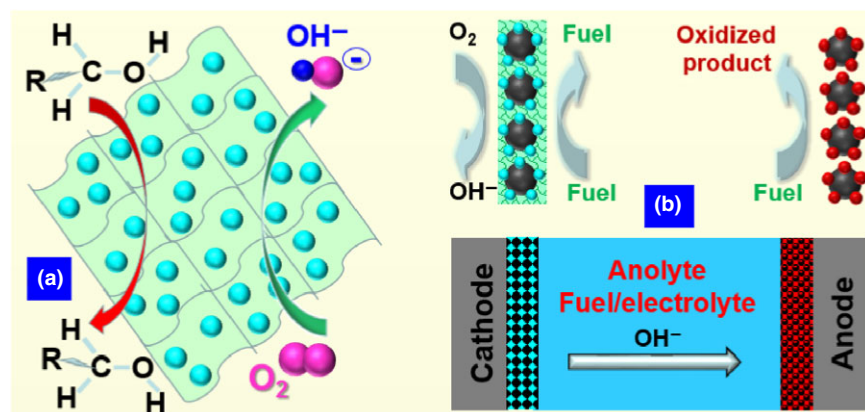
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sustain the conductivity of OH^- ions in the fuel. Therefore, KOH was always the primary option to be added to the anode fuel solution to form an anolyte.

Based on the above unique features, the catalyst-selective strategy provides a versatile approach for the development of membraneless DLFCs.[21,22,25] With a proper management of the catalyst selectivity in the cell, many small-molecular organics can be employed as fuels, for example, methanol, ethanol, ethylene glycol, glycerol, formats, and other small-molecule organics or their salts. In addition, the catalyst-selective strategy allows operation of the membraneless DLFCs without any manipulation of the non-mixture laminar flow of the fuel and air, enabling the development of power-generation devices in flexible configurations without dimensional limitations. With the inexpensive anode fuels and non-platinum cathode catalysts and without the need for an ion-change membrane and any fuel crossover issues, low-cost and scalable membraneless alkaline DLFC systems can be realized.

3. Selectivity of Catalysts with Respect to Their Activity for the Oxygen Reduction Reaction and Their Inactivity for the Fuel Oxidation Reaction

The catalyst-selective membraneless DLFC approach was originally inspired by an observed experimental phenomenon that the oxidation reaction of a small-molecule organic salt, potassium formate, does not occur on the

Figure 1. a) Schematic representation of a catalyst with a selective activity. b) Schematic of a membraneless alkaline direct liquid fuel cell operated with a catalyst-selective principle. Reproduced with permission from ref. [21] (Copyright 2016, Elsevier Publisher).

highly active ORR cathode catalysts, Pt/C (platinum on carbon support).[22a] As presented in **Figure 2**, on the Pd/C electrode, the oxidation current of HCOOK increases in a linear manner from −0.7 V to 0.1 V (vs SHE). This potential range matches the anode potential domain for the operation of alkaline DLFCs. However, as seen in
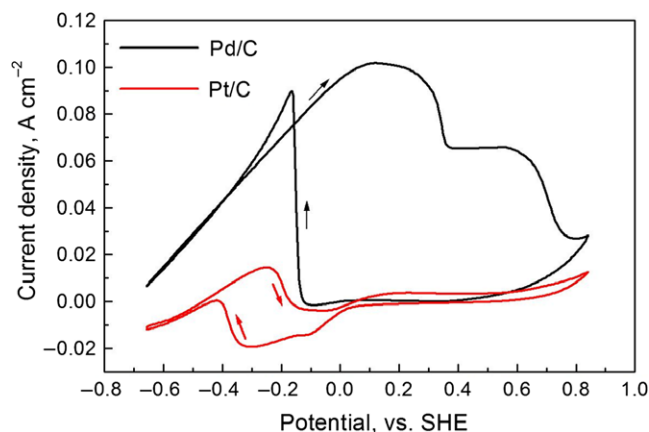

Figure 2. Cyclic voltammograms of Pd/C and Pt/C electrodes in an electrolyte containing 1.0 mol L^{-1} HCOOK in 1.0 mol L^{-1} KOH at 20 mV s^{-1}. Experiments were performed at ambient temperature. Reproduced with permission from ref. [22a] (Copyright 2015, Elsevier Publisher).
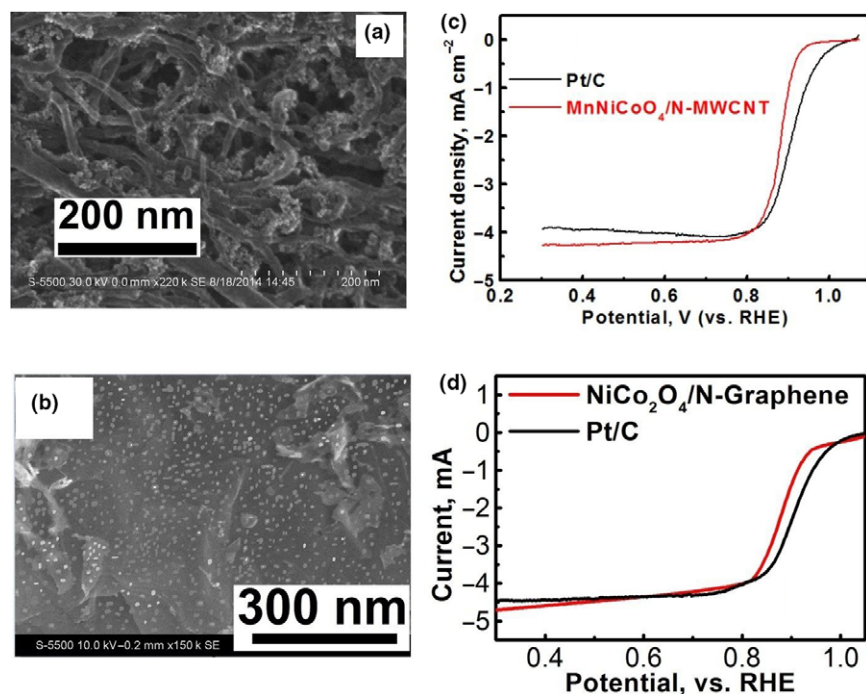

Figure 3. a) STEM image of the MnNiCoO$_4$/N-MWCNT catalyst. b) STEM image of the NiCo$_2$O$_4$/N-graphene catalyst. c) Rotating-disk electrode voltammetry profiles (at 1600 rpm, G-force 14) of Pt/C and MnNiCoO$_4$/N-MWCNT catalyst catalysts in 1.0 mol L^{-1} KOH solution saturated with O$_2$ (the scan rate is 5 mV s^{-1}). d) Rotating-disk electrode voltammetry profiles (at 1600 rpm, G-force 14) of Pt/C and NiCo$_2$O$_4$/N-graphene catalysts in 1.0 mol L^{-1} KOH solution saturated with O$_2$ (the scan rate is 5 mV s^{-1}). Reproduced with permission from ref. [22b] (Copyright 2015, Royal Society of Chemistry). Reproduced with permission from ref. [21] (Copyright 2016, Elsevier Publisher).

Figure 2, the oxidation current of HCOOK on the Pt/C catalyst is extremely low, implying an inactivity of the Pt/C for the oxidation of HCOOK. Therefore, the Pt/C shows an excellent catalytic selectivity in terms of its high activity for the ORR and its inactivity for the oxidation reaction of potassium formate.[22a]

After the successful demonstration of a membraneless direct formate fuel cell (DFFC) with the Pt/C cathode catalyst, other two less-expensive and highly selective ORR cathode catalysts were developed based on strongly coupled nanostructured carbon materials and transition-metal-oxide nanocrystals. The two catalysts are MnNiCoO$_4$/N-MWCNT (MnNiCoO$_4$ nanoparticles on a nitrogen-doped multiwall carbon nanotube, **Figure 3**a) and NiCo$_2$O$_4$/N-graphene (NiCo$_2$O$_4$ nanocrystals on an N-doped graphene, Figure 3b).[22] The ORR activity investigations with these two catalysts are, respectively, summarized in Figure 3c (MnNiCoO$_4$/N-MWCNT) and Figure 3d (NiCo$_2$O$_4$/N-graphene). Under the alkaline condition, the MnNiCoO$_4$/N-MWCNT and the NiCo$_2$O$_4$/N-graphene catalysts show ORR activity almost comparable to that of the Pt/C catalyst.

The activities of the MnNiCoO$_4$/N-MWCNT and the NiCo$_2$O$_4$/N-graphene catalysts for the oxidation reaction of methanol, ethanol, ethylene glycol, or glycerol have been comprehensively studied, as summarized with the experimental results in **Figure 4**.[22] For a comparison, a reliable anode catalyst, PtRu/C, has also been used as a control catalyst to demonstrate the FOR inactivity of the MnNiCoO$_4$/N-MWCNT and the NiCo$_2$O$_4$/N-graphene catalysts. On the PtRu/C electrode, the oxidation current of CH$_3$OH, CH$_3$CH$_2$OH, CH$_2$OHCH$_2$OH, or CH$_2$OH-CHOHCH$_2$OH increases in an almost linear manner within the selected potential range for the operation of the alkaline fuel cells (−0.6–0.1 V vs SHE). However, on the MnNiCoO$_4$/N-MWCNT (Figure 4a) and the NiCo$_2$O$_4$/N-graphene (Figure 4b) catalysts, there is almost no current for the oxidation reaction of CH$_3$OH, CH$_3$CH$_2$OH, CH$_2$OHCH$_2$OH, or CH$_2$OHCHOHCH$_2$OH liquid fuels throughout the selected potential domain.[22] A nickel sulfide Ni$_3$S$_2$ has also been reported as a highly selective catalyst, which exhibits a desired inactivity for the oxidation reaction of formate but can provide a high activity for the ORR.[25]

The mechanism with respect to the FOR inactivity of the MnNiCoO$_4$/N-MWCNT and the NiCo$_2$O$_4$/N-graphene catalysts for the oxidation of CH$_3$OH, CH$_3$CH$_2$OH, CH$_2$OH-CH$_2$OH, or CH$_2$OHCHOHCH$_2$OH is not clear so far. It is likely that the MnNiCoO$_4$/N-MWCNT and the NiCo$_2$O$_4$/N-graphene catalysts are not able to provide facile active sites for the chemical absorption of the liquid fuels. The relevant mechanistic studies should be focused in the future.

4. Membraneless DLFCs Enabled by the Catalyst-Selective Strategy

The membraneless alkaline DLFC concept has been validated with two recently developed low-cost non-Pt cathode catalysts MnNiCoO$_4$/N-
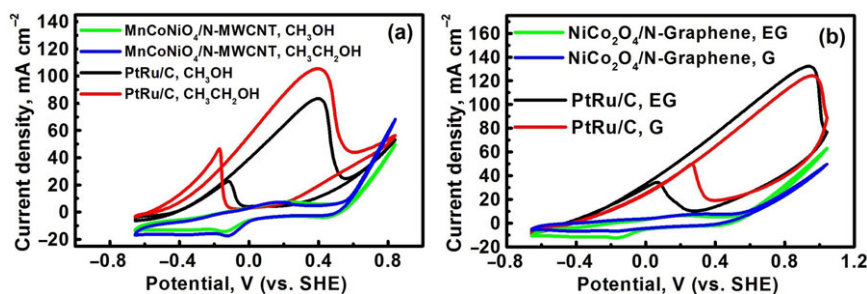
Figure 4. Cyclic voltammograms (10 mV s^{-1}) of a) the MnNiCoO$_4$/N-MWCNT and PtRu/C electrodes in the electrolyte containing either 1.0 mol L^{-1} CH$_3$OH in 1.0 mol L^{-1} KOH or 1.0 mol L^{-1} CH$_3$CH$_2$OH in 1.0 mol L^{-1} KOH, and b) NiCo$_2$O$_4$/N-graphene and PtRu/C electrodes in the electrolyte containing either 1.0 mol L^{-1} ethylene glycol (EG) in 1.0 mol L^{-1} KOH or 1.0 mol L^{-1} glycerol (G) in 1.0 mol L^{-1} KOH. Reproduced with permission from ref. [21] (Copyright 2016, Elsevier Publisher).

MWCNT and NiCo$_2$O$_4$/N-graphene, which exhibit an ORR activity comparable to that of Pt/C, but do not have an obvious catalytic activity for the FOR of methanol, ethanol, ethylene glycol, glycerol, or formats.[21,22b] By taking advantage of the catalytic selectivity, there have been five membraneless alkaline DLFC systems have been pursued and demonstrated so far: direct methanol fuel cell, direct ethanol fuel cell, direct ethylene glycol fuel cell, direct glycerol fuel cell, and DFFC.[21,22] These DLFCs were demonstrated with an in-house designed membraneless DLFC platform, as schematized in **Figure 5**.

Figure 6 presents the performances of the five membraneless alkaline DLFCs under the specifications and operating conditions as briefly described in **Table 1**. The key cell performance metrics (power density and current density at specific voltages) of the five DLFC systems are also summarized in Table 1. To run the fuel cells safely, as shown in Table 1, all the DLFCs are operated at temperatures below the boiling points of the fuels.

Based on the highly selective property (high ORR activity and FOR inactivity) of the MnCoNiO$_4$/N-MWCNT and NiCo$_2$O$_4$/N-graphene cathode catalysts, the fuel cell performance of the membraneless alkaline

Figure 5. Schematic of an in-house designed membraneless alkaline direct liquid fuel cell. Reproduced with permission from ref. [21] (Copyright 2016, Elsevier Publisher).

DLFCs illustrated in Figure 6 and Table 1 is comparable or even superior to those of traditional DLFCs with the proton- or hydroxide-exchange membranes.[26] In the traditional DLFCs, even with an H$^+$- an OH$^-$-exchange membrane, the anode fuel intrinsically tends to diffuse through the membrane to enter the cathode, where it is easily oxidized on the cathode. Such a fuel crossover has been recognized as one of the most significant challenges for operating the traditional membrane-based DLFCs.[27] Due to the FOR inactivity of the cathode catalysts, the membraneless DLFCs demonstrated in Figure 6 and Table 1 do not suffer any negative effect of the fuel crossover, thus showing enhanced performance in contrast to those traditional membrane-based DLFCs. In addition, as the catalyst-selective DLFCs does not have mixed potential concerns, the open-circuit voltages of the DLFCs demonstrated in Figure 6 and Table 1 are even closer to their theoretical value if compared to those of the traditional membrane-based DLFCs.[26,28]

5. Perspectives and Future Efforts

The catalyst-selective membraneless DLFCs eliminate the need for high-cost or technically unviable ion-exchange polymer membranes and expensive platinum-based cathode catalysts. The novel catalyst-selective strategy allows operation of the membraneless DLFCs without any manipulation of the non-mixture laminar flow of the fuel and air, enabling the development of energy-generation devices in flexible configurations without dimensional limitations. The catalyst-selective operating principle also allows the use of a variety of inexpensive, renewable liquid fuels. All the above unique features make the membraneless DLFC systems attractive for a broad range of applications, such as portable power sources, transportation, and stationary energy-generation systems. It is expected to have a significant impact on clean energy technologies and benefit the society from an economical and environmental point of view.

However, although the validated membraneless DLFC examples presented in Section 4 provide clear advantages and superiority of the "catalyst-selective strategy," the development of this proof-of-concept platform to a viable technology needs intensive research and development efforts. Future research directions and efforts are suggested as below:

- Although the MnCoNiO$_4$/N-MWCNT and NiCo$_2$O$_4$/N-graphene cathode catalysts have been verified to have an excellent catalytic selectivity, there is a desire and an expectation to develop/design highly selective cathode catalysts with low-cost components. In addition to exploring the catalysts, the relevant mechanisms regarding their ORR activity and FOR inactivity should be rigorously investigated with electrochemical, microscopic, and spectroscopic techniques, as well as computational simulations.
- So far, all the membraneless DLFCs have been demonstrated with well-developed, relatively reliable anode catalyst systems for each specific fuel. These catalysts are still based on noble metals. Low-cost, non-noble-metal anode catalysts should be
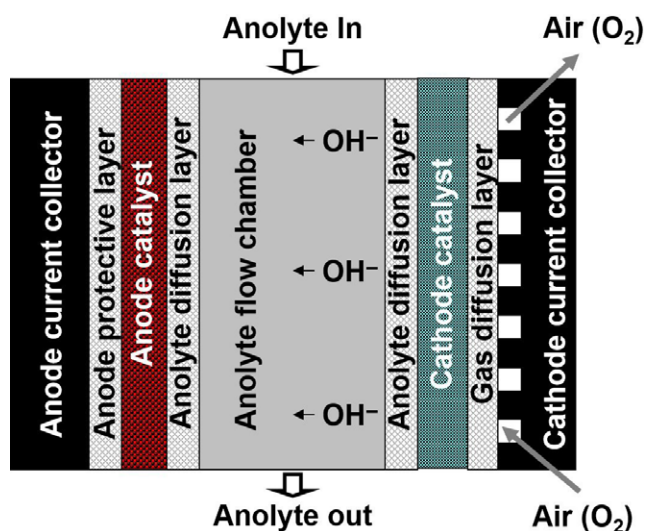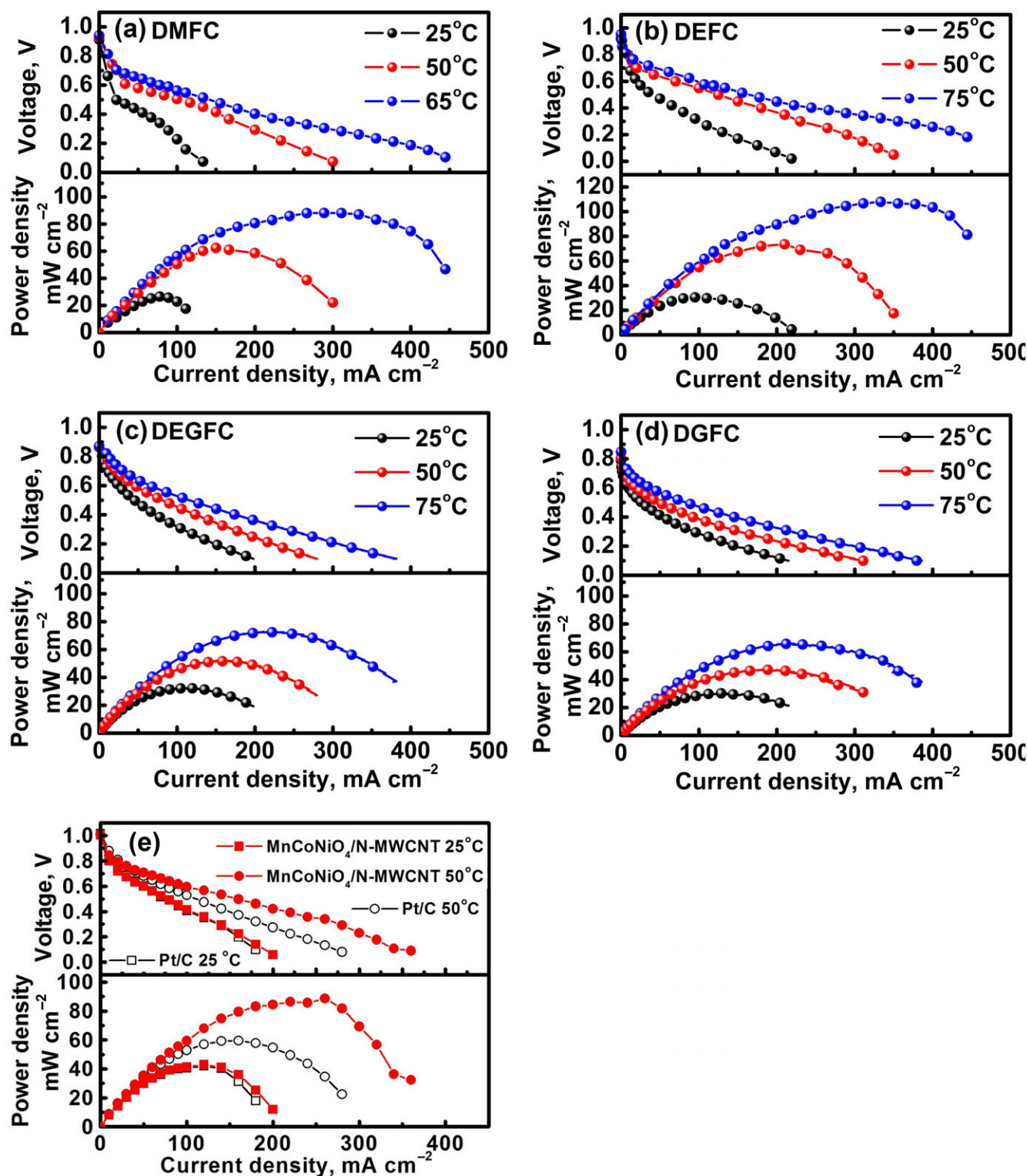
Figure 6. Polarization curves and corresponding power plots of the membraneless alkaline direct liquid fuel cells operated at different temperatures: a) direct methanol fuel cell (DMFC), b) direct ethanol fuel cell (DEFC); c) direct ethylene glycol fuel cell (DEGFC); d) direct glycerol fuel cell (DGFC) and e) direct formate fuel cell (DFFC). Reproduced with permission from ref. [21] (Copyright 2016, Elsevier Publisher) and ref. [22b] (Copyright 2015, Royal Society of Chemistry). DEFC, direct ethanol fuel cell; DEGFC, direct ethylene glycol fuel cell.

Table 1. Summary of the specifications and performances of membraneless alkaline DLFC systems.

Membraneless fuel cell system	Fuel/anolyte	Cathode catalyst	Anode catalyst	Maximum power density, mW cm^{-2}	Current density at 0.55 V, mA cm^{-2}
DFFC	HCOOK/KOH	MnCoNiO$_4$/N-MWCNT	Pd/C	>90 at (50 °C)	~150
DMFC	Methanol/KOH	MnCoNiO$_4$/N-MWCNT	PtRu/C	>90 at (65 °C)	~100
DEFC	Ethanol/KOH	MnCoNiO$_4$/N-MWCNT	PtRu/C	>100 (at 75 °C)	~150
DEGFC	Ethylene glycol/KOH	NiCo$_2$O$_4$/N-graphene	PtRu/C	>80 (at 75 °C)	~100
DGFC	Glycerol/KOH	NiCo$_2$O$_4$/N-graphene	PtRu/C	>70 (at 75 °C)	~70

DEFC, direct ethanol fuel cell; DEGFC, direct ethylene glycol fuel cell; DFFC, direct formate fuel cell; DGFC, direct glycerol fuel cell; DLFC, direct liquid fuel cell; DMFC, direct methanol fuel cell.

explored for the specific fuels in the future. Due to the super-low solubility and diffusivity of oxygen in alkaline electrolytes, the catalytic selectivity at the anode of the membraneless alkaline DLFCs is not an obligation. Evaluation of the anode catalysts should be mainly focused on their FOR activity for specific fuels.

- From a practical or an engineering point of view, to achieve membraneless DLFCs with high power and energy density at an affordable cost, the cell configurations and operating conditions should be optimized. The optimization of anode/cathode structure and catalyst loadings can follow the relevant strategies similar to those of the traditional membrane-based liquid fuel cells. In particular, for the membraneless DLFCs, the following additional aspects need to be rigorously optimized: 1) Composition and concentration of the anolyte (the mixture of fuel and supporting electrolyte) as well as their flow rates, which are critical for the mass transfer of the fuel and supporting electrolyte; they will also influence the fuel utilization efficiency. 2) The thickness of the anolyte layer is also an important parameter to be optimized; a thinner anolyte layer will reduce cell impedance but will increase the risk of oxygen diffusion to the anode. 3) Air flow rate and back pressure at the cathode also have opposing effects on cell performance; high flow rate and high back pressure would enhance the diffusivity of oxygen in the cathode gas diffusion layer but would increase the risk of oxygen diffusion to the anode. 4) Other operating conditions, such as temperature and structure of anode catalyst layer to improve fuel efficiency.

- One potential challenge for the development of the membraneless alkaline DLFCs lies in the possible poisoning of the electrolyte by CO_2. In addition to the CO_2 from ambient air similar to the common issue associated with the traditional alkaline fuel cells, the oxidation of the liquid anode fuel introduces an additional source of electrolyte carbonation (CO_2-generated in situ). The CO_2 issue from ambient air at the cathode can be easily mitigated by purifying the air with a "CO_2-scrubber." For the in situ-generated CO_2, additional technical approaches need to be developed. The following technical strategies may help 1) replenishing the anolyte on a regular maintenance schedule; 2) applying a "CO_2–absorption layer" at the anode; and 3) regenerating the anolyte intermittently by employing a proper filter filled with the Ca^{2+}-ion or Mg^{2+}-ion salts. It may need comprehensive efforts from the alkaline fuel cell community to address the relevant issues regarding the in situ-generated CO_2 as it is a commonly important challenge of the alkaline DLFCs.

6. Conclusions

A recently proposed catalyst-selective strategy opens a promising pathway for the advancement/validation of DLFC technologies. The central idea of this novel strategy is employing a highly selective cathode catalyst that catalyzes only the ORR but does not catalyze the oxidation reaction of a specific fuel. Therefore, during the operation of DLFCs, the fuel can enter the cathode freely without the need for an ionic membrane in the cell. This unique catalyst-selective strategy tactically avoids the employment of expensive cathode catalysts and the use of high-cost or practically unviable ionic polymer membranes. In addition, the catalyst-selective operating principle overcomes the scalability issue of the traditional laminar-flow membraneless DLFCs. With proper management of the catalyst selectivity in the cell, a number of inexpensive, renewable small-molecular organics can be employed as anode fuels. This catalyst-selective approach of membraneless alkaline DLFCs can enable the development of inexpensive energy-generation systems for portable, transportation, and stationary applications. However, the development of this concept to a transformative platform needs intensive research and development efforts. Future research efforts are suggested to focus on the exploration of low-cost highly selective cathode catalysts and investigation of the mechanism of their catalytic selectivity, development of low-cost anode catalysts for specific liquid fuels, optimization of cell configurations and operating conditions, and addressing the CO_2 contamination problems.

Conflict of Interest

The authors declare no conflict of interest.

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