Direct Ammonia Alkaline Anion-Exchange Membrane Fuel Cells

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On-board hydrogen storage remains a big challenge for fuel cell powered electric vehicles. Ammonia contains 17.6 wt % hydrogen and has been recognized as a potential on-board vehicular hydrogen media. Direct ammonia fuel cells are interesting because they do not require an ammonia cracking process to produce hydrogen, whereas conventional proton exchange membrane fuel cells based on acidic membranes such as Nafion are not compatible with NH₃. Here we report the operation of direct ammonia alkaline anion-exchange fuel cells based on low cost membrane and non-noble catalysts with potential use in transportation and other applications.

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Hydrogen economy is an excellent idea in terms of climate change, but on-board hydrogen storage remains a big challenge. Alternatively, hydrogen can be stored in light chemicals such as ammonia, methanol, or methane which contain 17.6, 25.0, and 12.5 wt % hydrogen, respectively, in their molecules. Unlike methanol, ammonia is carbon-free at the end users, which makes it an ideal fuel for fuel cells as low emission power supply. Ammonia is a cheap basic chemical (~U.S. $200 per ton) which is produced over 100 million tons per annum and is commonly used in the industry and agriculture. The main drawback of ammonia is its toxicity, but it does have several advantages over hydrogen, hydrocarbons, and alcohols. Similar to hydrogen, ammonia is mainly produced from fossil fuels, but this is a centralized process and the yielded CO₂ can be stored by sequestration. The conversion of natural gas to ammonia is about 60–65% energy-efficient which is just slightly lower than for hydrogen production from reforming of natural gas (65–75%). In the long run, ammonia can be produced from biomass or renewable electricity through an electrochemical synthesis process for low carbon emission.

Conventional proton exchange membrane fuel cells (PEMFCs) based on an acidic membrane such as Nafion are not compatible with ammonia (~<0.1 ppm) and, hence, an on-board storage system based on ammonia would require a cracking reactor with a significant energy input with a large mass and volume plus extra costs. The present approach for the use in ammonia for conventional PEMFCs is to convert ammonia to hydrogen and nitrogen at high temperatures. It has also been reported that hydrogen can be produced from ammonia by electrolysis to then use the hydrogen in conventional PEMFCs, but this would consume some electricity generated by the fuel cell, thus decrease overall efficiency. From this point of view, to generate electricity directly from ammonia would be more efficient. Ammonia has also been investigated as a fuel for high temperature solid oxide fuel cells (SOFCs); however, SOFCs are in general not suitable for transport application due to the slow startup and brittleness of ceramic components.

Ammonia has been reported as a fuel for fuel cells based on KOH solution electrolyte as early as 1960s. Recently Hejze et al. reported that ammonia can be used for molten hydroxide (NaOH/KOH) fuel cell at a working temperature of 200–450°C. However, similar to conventional alkaline fuel cells, the durability of ammonia fuel cells operating with KOH-based electrolytes would be a critical issue due to the reaction between KOH and CO₂ if “free” air is used as oxidant.

Recently, alkaline membrane fuel cells have attracted the attention of researchers in the fuel cell society. Unlike conventional fuel cells based on acidic polymer electrolytes, inexpensive nonprecious catalysts (such as nickel, silver, MnO₂) can be used in alkaline membrane fuel cells. Presently available alkaline membranes are mainly based on organic quaternary ammonium hydroxide linked to polymers. It has been reported that this type of alkaline membrane are compatible with CO₂ and the introduction of CO₂ at the cathode can improve the fuel cell performance, therefore air can be directly used in a fuel cell. Recently, we have developed direct urea/urine fuel cells based on an alkaline anion-exchange membrane. In this article, room-temperature direct ammonia fuel cells based on alkaline membrane electrolyte have been demonstrated. Non-noble catalysts such as nickel and MnO₂ are used as catalysts.

Experimental

In our experiments, three alkaline membrane fuel cells were constructed based on alkaline membrane electrolytes.

Cell A: The blend membrane was made of a commercial strong anion-exchange resin (AER) (Amberlith IRA400, hydroxide form, ion-exchange capacity 1.46 meq/g, Aldrich) and poly(vinyl alcohol) (PVA), (MW 50,000, Aldrich) with a weight ratio of 50/50. PVA was dissolved in deionized water and stirred at 85°C for 2 h to form a gel. After the gel was cooled down to room temperature, the commercial resin was crushed into a powder with an agate mortar, mixed with PVA gel, casted on a glass plate and dried in a vacuum oven at room temperature to form the membrane.

Membrane electrode assemblies for the fuel cell measurements were fabricated with a MnO₂/C (20 wt % MnO₂) cathode, PtRu/C anode and AER-PVA blend membrane. MnO₂/C (20 wt %) was prepared from KMnO₄, Mn(CH₂COO)₂ and carbon (Cabot Vulcan XC-72R) by a coprecipitation method. PtRu/C (60 wt %, E-TEK) was used as anode. The loading of MnO₂ at the cathode and PtRu at the anode were 20 mg/cm² and 1 mg/cm², respectively. Carbon papers (Toray 090, water-proofed for anode, plain for cathode, E-TEK) were used as current collectors.

Cell B: Cr-decorated Ni (CDN) was prepared from NiCl₂·6H₂O, CrCl₃·6H₂O and KBH₄. The molar ratio of Ni to Cr was 97.7:2.3. Some trisodium citrate was added into the mixed NiCl₂/CrCl₃ aqueous solution to form a complex to decrease the reaction speed of reduction induced by the introduction of the KBH₄ solution (nickel particle size ~6 nm observed by transmission electron microscopy, not displayed). The nickel was dried at room temperature only. The as-prepared CDN was mixed with carbon to be used as anode. The same AER-PVA membrane and MnO₂/C cathode as in Cell A were used, but 50 wt % CDN/C was used at the anode with a loading of 10 mg/cm². The rest is the same as in Cell A.

Cell C: The main part of the alkaline membrane used in Cell C was chloroacetyl poly(2,6-dimethyl-1,4-phenylene oxide) (CPPO) synthesized from chloroacetyl chloride and poly(2,6-dimethyl-1,4-phenylene oxide) based on a method described by Wu et al. The mechanical strength of CPPO is unsatisfactory and it is difficult to form a dense membrane. The synthesized CPPO was then blended with PVA with a weight ratio of 50/50. The casted membrane was...
put in trimethylamine for 24 h for cross-linking followed by 24 h in a 2 mol L$^{-1}$ KOH aqueous solution before being used as an electrolyte. The MnO2 and CDN electrodes were the same as in Cell B.

Wet hydrogen, aqueous ammonia solution and ammonia gas were used as fuels for the fuel cell test and wet oxygen/air as the oxidant in the cathode. The hydrogen and oxygen/air were passed through room-temperature water, ammonia gas through saturated ammonia solution before entering the fuel cell. For the ammonia solution fuel cell, 35 wt % aqueous ammonia solution was pumped into the cell by a peristaltic pump. The effective cell area was 1 cm$^2$. A Solartron 1287A electrochemical interface coupled with the CorrWare/CorrView software package was used to measure the fuel cell performance.

**Results and Discussion**

A diagram of the operating principle of direct ammonia fuel cells based on an alkaline electrolyte is shown in Fig. 1. At the cathode, oxygen is reduced to OH$^-$ ions in the presence of water, as in other alkaline fuel cells. This yields hydroxide ions which then transfer to the anode and react with ammonia to form nitrogen and water

$$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4 \text{OH}^- \quad (\text{cathode reaction}) \quad E^\circ = + 0.40 \text{ V}$$

$$2\text{NH}_3 + 6 \text{OH}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O} + 6 \text{e}^- \quad (\text{anode reaction}) \quad E^\circ = - 0.77 \text{ V}$$

$$4\text{NH}_3 + 3 \text{O}_2 \rightarrow 2 \text{N}_2 + 6\text{H}_2\text{O} \quad (\text{overall reaction}) \quad E^\circ = + 1.17 \text{ V}$$

The theoretical open-circuit voltage (OCV) of a NH$_3$/O$_2$ fuel cell is 1.17 V at 25°C which is slightly lower than the 1.23 V for a H$_2$/O$_2$ fuel cell under the same condition. However, the theoretical efficiency of an ammonia fuel cell is 88.7% at 25°C which is slightly higher than for a H$_2$/O$_2$ fuel cell (83.1% at 25°C). Water management, particularly at the cathode is another issue for conventional PEMFCs with a working temperature of ~80°C. In an alkaline membrane fuel cell, water is produced at the anode, therefore flooding at the cathode is expected to be less serious; however, water is produced at the anode which may dilute the fuel and flood the anode. Deep investigation is therefore required.

Figure 2a shows the OCV change against time for Cell A when PtRu/C was used as the anode and MnO$_2$/C as the cathode. An initial OCV of 0.28 V was observed in air. This is believed to correspond to the potential difference between the PtRu/C anode and the MnO$_2$/C cathode. When wet hydrogen was introduced at the anode side, the OCV increased immediately, indicating that PtRu/C is an active catalyst for H$_2$/O$_2$ fuel cells with an alkaline media. After the H$_2$/O$_2$ fuel cell tests, 35 wt % of aqueous ammonia solution was introduced into the cell. The initial OCV of 0.55 V is caused by the residual H$_2$ at the anode. After the introduction of aqueous ammonia solution, the OCV started to increase and reached an equilibrium after half an hour, indicating that the kinetic process is not very fast. However, the OCV of a NH$_3$/O$_2$ fuel cell is about 100 mV higher than for a H$_2$/O$_2$ fuel cell based on the same components.

The H$_2$/O$_2$ and NH$_3$/H$_2$O/O$_2$ fuel cell performances for Cell A are shown in Fig. 2b. For the H$_2$/O$_2$ fuel cell, a maximum current and power densities of 2.8 mA/cm$^2$ and 0.57 mW/cm$^2$ were achieved at room temperature. As for the NH$_3$/H$_2$O/O$_2$ fuel cell, both current and power densities were slightly higher than for a H$_2$/O$_2$ fuel cell which benefits from the higher OCV. Although the theoretical OCV of a H$_2$/O$_2$ fuel cell is higher than a NH$_3$/O$_2$ fuel cell (applicable as well for a NH$_3$/H$_2$O/O$_2$ fuel cell), the real OCV
of a cell could be different due to the difference in the catalytic activities of both electrodes which are related to the polarization losses at the electrodes, particularly at lower temperatures. Lower OCVs were also observed on direct alcohol alkaline membrane fuel cells using Pt/C as both electrodes. Other possibilities are the unoptimized methods for the electrode preparation and the possible cross diffusion of the fuel/oxidant through the membrane. These experiments indicate that a direct ammonia fuel cell at room temperature based on alkaline membrane is viable while achieving a comparable performance to hydrogen fuel cells.

It has been reported that inexpensive CDN is a good anode for alkaline membrane fuel cells. CDN was also prepared in our laboratory to replace the PtRu/C anode in ammonia fuel cells. As in Cell A, MnO2/C was used as the cathode. In Cell B, the oxidant was changed from wet oxygen to wet air. As shown in Fig. 3a, the initial OCV is about 0.27–0.3 V which is the potential difference between CDN and MnO2 (subtract electrode polarization). After the introduction of ammonia gas or solution, the OCV started to increase and reached an equilibrium after about 8 min which is shorter than the 30 min observed (Fig. 2a) when the PRu/C anode was used, indicating that CDN exhibits a kinetic process. The OCV is higher when 35 wt % aqueous ammonia solution was used as the fuel, possibly due to the better interface at the anode due to the diffusion of ammonium hydroxide. In fact, the ionized NH3·H2O would provide OH− ions and the OH−/e− mixed conduction would take place at the anode and therefore decrease the anode polarization leading to a slightly higher overall OCV than for ammonia gas. The higher initial OCV for hydrogen is due to the residual ammonia. It took a while to reach an equilibrium when hydrogen was used as the fuel. The oscillation of the OCV for hydrogen might be related to the bubble at the electrodes.

The fuel cell performance of Cell B is shown in Fig. 3b when wet hydrogen, wet ammonia gas, and 35 wt % aqueous ammonia solution were used as the fuels. Compared to Cell A (Fig. 2b), the OCV is just slightly lower when hydrogen or ammonia solution was used as the fuel. This is usual as instead of oxygen was used at the cathode. However, both the current and power densities are much higher in Cell B due to the use of nanosized nickel-based anode (Fig. 3b). A maximum power density of 9 mW/cm2 has been achieved when 35 wt % aqueous ammonia solution was used as the fuel, wet air as the oxidant. When gaseous ammonia solution was used as the fuel, the OCV was similar to hydrogen and the power density is slightly lower. The slightly higher performance when 35 wt % aqueous ammonia solution was used is possibly related to the possible lower anode polarization due to the OH−/e− mixed conduction as mentioned above. Possibly it is also related to the better cross diffusion of the anode or/and anode/electrode interface when a liquid fuel was used. A better performance was observed when nanosized CDN was used, which is also related to the higher loading of catalysts.

The second alkaline membrane we used for the fuel cell tests was CPPO. The synthesis process was the same as reported by Wu et al. A CPPO-PVA blend membrane was used as electrolyte. MnO2/C and CDN/C was used as the cathode and anode, respectively. The fuel cell performance of Cell C is shown in Fig. 4 when wet hydrogen and wet ammonia gas were used as the fuels. A maximum power density of 16 mW/cm² has been achieved when ammonia was used as the fuel, wet oxygen as the oxidant. The power density can be further improved with optimization of the composition and the microstructure of the electrodes.

Conclusions

Direct ammonia alkaline membrane fuel cells based on low cost membrane electrolytes and non-noble catalysts such as MnO2 and CDN have been demonstrated. The nanosized nickel catalysts (−6 nm) exhibited a higher catalytic activity than PtRu/C although with a higher loading but overall cost would still be much lower. For the same cell, the OCV and power density for a direct ammonia fuel cell were slightly higher than those when hydrogen was used as the fuel.
fuel. The development of low temperature direct ammonia fuel cells based on alkaline membranes and inexpensive catalysts is still at an early stage. With further optimization, this type of fuel cell has the potential to power electrical vehicles if a high power density and safe control of the ammonia can be achieved.

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References