100–200 °C polymer fuel cells for use with NaAlH$_4$

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Abstract

The complex hydride NaAlH$_4$ is attracting much attention right now because of high hydrogen storage capacity and a practical desorption temperature that can be brought down below 150 °C. However, this is still far from the working temperature of conventional perfluorosulfonic acid based polymer fuel cells (e.g. Nafion cells). A hydrogen desorption temperature below 80 °C is mandatory if the excess heat of such a fuel cell shall be used for hydrogen desorption from a NaAlH$_4$ storage system. Our approach is to increase the working temperature of the polymer fuel cell. The present paper reports our recent work on polymer fuel cells operating at temperatures up to 200 °C. The key component to make this possible is an electrolyte membrane of polybenzimidazole (PBI) doped with phosphoric acid. Cells are operated at temperatures up to 200 °C without any humidification. Continuous service for more than 6 months at 150 °C is demonstrated. The temperature and amount of the excess heat is more than enough to run a metal hydride tank based on NaAlH$_4$.
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1. Introduction

Metal hydride systems for use at near ambient temperature and pressure generally suffer from a low gravimetric hydrogen storage capacity. Hydride systems with much higher capacities are known, but only with higher working temperatures like MgH$_2$ with 7.6 wt.% at 300 °C. The working temperature of the metal hydride is an important issue. Not only must the hydride be heated to the working temperature, but a significant amount of heat (the desorption enthalpy) must also be supplied at this temperature. This heat can be produced by burning part of the stored hydrogen, but in case of MgH$_2$ at least 31% of the stored hydrogen will then be wasted just to provide heat for hydrogen desorption. When fuelling a fuel cell, a more effective way is to make use of the heat that is always produced by the fuel cell along with the electricity. Therefore, the working temperature of the hydride should not be higher than the working temperature of the fuel cell. Conventional proton exchange membrane fuel cells (PEMFC) have a working temperature of about 80 °C, and

consequently, a compatible metal hydride system must have an equilibrium pressure of at least 1 bar and sufficient desorption kinetics, at temperatures significantly below 80 °C. During recent years several groups have reported reversible hydrogen storage capacities in the range of 3–5 wt.% and release temperatures in the range of 100–200 °C for NaAlH$_4$ [1–3]. A further temperature reduction down below 80 °C has not proven easy. Why not increase the temperature of the PEMFC instead?

The electrolyte of a normal PEMFC is a perfluorinated sulfonic acid polymer membrane (e.g. Nafion), which is only proton conductive with high water content. This is the reason why the working temperature cannot easily be raised above 100 °C. For a high-temperature system, another membrane material is needed. In 1995, Wainright and co-workers [4] proposed phosphoric acid doped polybenzimidazole (PBI) as a high-temperature proton conductor, and our group has followed that line [5,6]. Other high-temperature membranes under development have been reviewed recently [7]. The driving force for the development of high-temperature PEM fuel cells has to a large extend been to increased the tolerance to carbon monoxide (over three orders of magnitude at 200 °C [8]) and consequently the possibility of powering the fuel
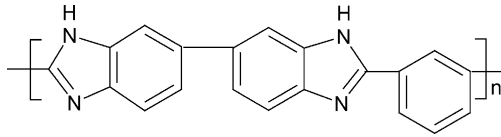
Fig. 1. The repeating unit of the PBI, poly 2,2′-*m*-(phenylene)-5,5′-bibenzimidazole.

cell directly from a reformer/shift reactor without purification [9]. However, in this paper the focus is on the possible interplay with complex hydrides like NaAlH$_4$. The high operating temperature offers an excellent opportunity for improving the energy efficiency by using the excess heat for hydrogen desorption.

2. Experimental

The PBI used in this work was poly-2,2′-*m*-(phenylene)-5,5′-bibenzimidazole (see Fig. 1) obtained from Celanese or later synthesized [10]. After casting to a thickness of about 50 μm, the membrane was doped with phosphoric acid to a level of 5–6 H$_3$PO$_4$ molecules per repeat unit of PBI. The catalyst applied was platinum on carbon, about 0.5 mg/cm^2 for all electrodes. The experimental details are given elsewhere [6,10].

3. Results

The ionic conductivity of acid doped PBI was measured earlier [10] and the value is plotted as a function of temperature and relative humidity in Fig. 2. It can be seen that the conductivity at 200 °C and only 5% relative humidity is similar to that of Nafion at 80 °C and 90% relative humidity. Even at very low relative humidity ,the conductivity of doped PBI is still significant. In contrast, the conductivity of Nafion depends on a very high relative humidity and that is the reason why Nafion cannot easily be applied at higher temperatures than 80 °C. In Nafion, the proton conduction mechanism involves transport of several water molecules with the proton (the water drag). This implies that the membrane is depleted in water on the anode side as the water molecules are "dragged" towards the cathode with the protons. This
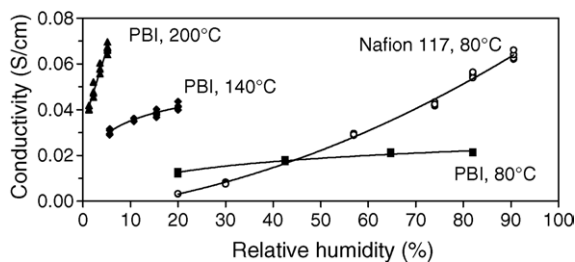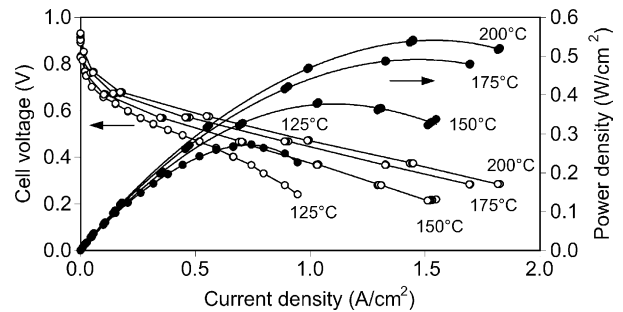

Fig. 3. Polarization curves and power curves for a single cell operated on hydrogen and oxygen, both at atmospheric pressure. The active electrode area was 10 cm^2 with a platinum loading of 0.5 mg/cm^2. No humidification was applied [8].

depletion or drying out leads to a loss of conductivity unless water is continuously supplied in a controlled amount with the reactant gasses (water management). In contrast to Nafion, PBI has a water drag number of zero or close to zero [11,12] meaning that practically no water molecules are transported with the proton. It is evident from Fig. 2, however, that the water content still affects the conductivity and that a certain amount of water is desired in the membrane, but this is easily maintained via diffusion of water produced at the cathode as result of the overall process in the fuel cell. As a result, PBI based fuel cells can run on dry gasses.

Fig. 3 shows polarization curves at different temperatures for a single cell with a PBI membrane. The cell was in all cases operated without any humidification, i.e. on dry gasses. A number of lifetime experiments are being carried out with single cells at different temperatures. The results so far are plotted in Fig. 4. The cells were operated on hydrogen and oxygen at a constant potential of 0.5 V. A three-cell stack was constructed as described above with an active area of 100 cm^2 on each electrode. Testing was performed at 200 °C with hydrogen and oxygen at ambient pressure. The polarization and power behaviour is shown in Fig. 5. During testing a significant heat evolution was observed, especially at high currents, and as the stack was constructed without cooling the system had to be prevented from overheating by interruption of the current. The lack of proper cooling made it difficult to obtain reliable steady measurement at high currents and the curves in Fig. 5 are interrupted at 110 A. However, currents
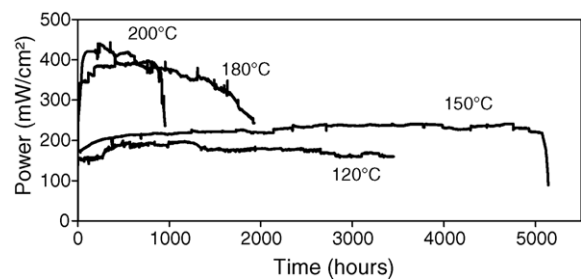

Fig. 2. Conductivity of PBI doped with 5.6% phosphoric acid. Measurements for Nafion-117 are added for comparison [10].

Fig. 4. Lifetime tests at different temperatures. Cells of 5 cm^2 tested at 0.5 V with hydrogen and oxygen at ambient pressure.
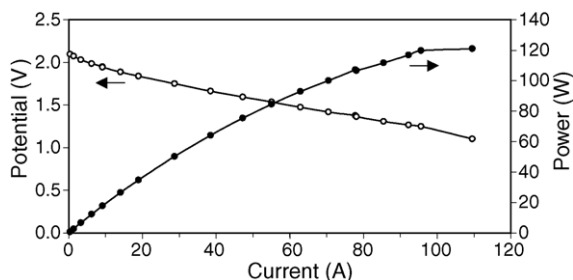
Fig. 5. Polarization curves and power curves for a three-cell stack at 200 °C operated on hydrogen and oxygen, both at atmospheric pressure. The active area was 100 cm² on each electrode and no humidification was applied.
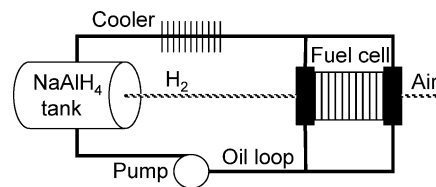

Fig. 6. An alanate/elevated temperature PEM fuel cell system schematically. An oil loop is transferring heat from the fuel cell to the alanate tank. The "cooler" could be a heat exchanger for optional further cooling.

of over 150 A (1.5 A/cm²) were measured accompanied by a moderate temperature increase.

4. Discussion

At standard temperature and pressure hydrogen fuel cells have a maximum electrical efficiency of 95% based on the lower heating value or 83% based on the higher heating value. However, the practical electrical efficiency depends on the cell load and is only about 50% or less. The remaining 50% or more is converted into heat. At 200 °C, only the lower heating value of -244 kJ/mole H_2 is relevant. Fifty percent of that is -122 kJ/mole H_2.

Hydrogen desorption from $NaAlH_4$ occurs in two steps. Bogdanovic et al. [13] determined the desorption enthalpy for $NaAlH_4/Na_3AlH_6$–Al to 37 kJ/(mol H_2) and for Na_3AlH_6/NaH–Al to 47 kJ/(mol H_2) from van't Hoff lines. The first step provides 1 mol of H_2 and the next step only half a mole H_2 and the resulting weighted average is then 40 kJ/(mol H_2). This corresponds to 16% of the hydrogen fuel. A system with a low temperature PEMFC operating at 50% electrical efficiency will then only perform at 42% overall efficiency. These figures represent the ideal thermodynamic case with no losses on the heat transfer. In practice there will be significant heat losses to the surroundings and the overall loss will be higher. A 200 °C fuel cell operating at 50% electrical efficiency will produce 122 kJ heat per mole H_2 consumed. This is three times the amount required for desorbing 1 mol H_2, and even with significant heat losses enough heat will be available. Consequently, no hydrogen needs to be burned for providing the desorption heat and the overall efficiency is still 50% in contrast to 42% or lower for the low temperature fuel cell.

A possible system integrating a $NaAlH_4$ tank with a HT–PEMFC is shown schematically in Fig. 6. If the alanate is operating at 150 °C and the fuel cell at 200 °C, a temperature difference of 50 °C is available as a driving force for the heat transfer. A cooler (or a heat exchanger) is added in the oil loop to allow for further cooling when necessary.

The equilibrium desorption pressures for $NaAlH_4$ (first step) and Na_3AlH_6 (second step) are 60 and 3 bar,

respectively, at 150 °C [13]. This means that both steps can be exploited with sufficient desorption pressures provided the kinetics are fast enough. Several groups have performed kinetic measurements. An example is the Arrhenius plots of Sandrock et al. [3] for $TiCl_3$ doped $NaAlH_4$ desorbing into an evacuated chamber. Reading the desorption rates at 150 °C gives 12 and 0.5 wt.%/h, respectively, for first and second steps. General rate predictions based on specific experiments are dangerous as kinetics depends on many factors, like particle size, heat transfer, catalytic activity and state of charge. However, the measurements show that the first step at which most of the reversible hydrogen (up to 3.7 wt.%) is released can be fast at 150 °C. Assuming a constant rate of 12 wt.%/h 3.7 wt% can be discharged in less than 20 min. The second and slower step of up to 1.9 wt.% will then take about 4 h. These predictions are only meant to give an idea of possible practical discharge times and further improvements are expected.

Finally, PBI has been long known for many applications including garments for firemen. It has a potential for cheap manufacturing without the environmental problems related with the use of fluorine (in contrast to the perfluorinated polymers).

5. Conclusion

The problem of temperature mismatch between conventional Nafion based polymer fuel cells and the high capacity metal hydride systems like $NaAlH_4$ can be overcome with the use of a high-temperature polymer, in this case polybenzimidazole (PBI). It is shown that polymer fuel cells based on PBI can be operated at temperatures up to 200 °C. Long term experiments have shown a lifetime of more than 6 months at 150 °C. In contrast to Nafion cells PBI cells need no humidification of the gases. This simplifies the operation and the construction of the peripheral system. Application of a fuel cell system able to release the excess heat at a temperature higher than the desorption temperature of the metal hydride system allows for a significant improvement of electrical efficiency as no fuel need to be used purely for hydrogen desorption. Finally, A simple system comprising an alanate tank and a 200 °C PEMFC heat integrated via an oil loop is suggested. The plateau pressures for the first and second plateaus of $NaAlH_4$ are both well above ambient

pressure at 150 °C, and thus high enough to power a fuel cell directly.

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