

Short Communication

Investigation of M_2HPO_4 ($M= K^+, Na^+$) as Electrolyte for Alkaline Fuel Cell Working with Oxygen Containing Carbon Dioxide

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Basic salt of hydrogen phosphate (M_2HPO_4) was investigated as electrolyte for alkaline fuel cell (AFC). A maximum power density (MPD) of 60 mW cm^{-2} was obtained with K_2HPO_4 saturated solvent at room temperature, and a MPD of 30 mW cm^{-2} was observed with Na_2HPO_4 . The fuel cell with K_2HO_4 can work at least 3600s without significant performance decrease. More interestingly, the electrolyte shows considerable CO_2 tolerance since no obvious performance drop was observed when CO_2 of purity of 99% was introduced into the oxygen stream. The results may provide an alternative way to develop electrolyte for AFC that is tolerant to CO_2 .

Keywords: alkaline, electrolyte, fuel cell, hydrogen phosphate

1. INTRODUCTION

Fuel cells have been described as clean, quiet and efficiency power source to solve the environmental and energy sources problems haunting the world for decades [1-6]. Till now several types of fuel cells have been developed, of which the alkaline fuel cell (AFC) has succeeded in working as power source for space ship as early as in 1960s and is now one of the most sophisticated fuel cells. The commonly applied electrolyte for alkaline fuel cell is KOH and NaOH, this electrolyte is high in ionic conductivity (540 mS cm^{-1}) [7].

However, the alkaline electrolyte reacts easily with CO₂ and carbonate with low solubility is generated and deposit on the electrode and electrolyte. The deposition shall plug pores in gas distribution layer and the active layers shall get mechanically disrupted, and the fuel cell performance is jeopardized. This problem gets more serious since CO₂ is one of the products of the fuel cell reaction especially when the methane or ethanol is fed as fuel. As a result, alkaline fuel cell can not work with air, which contains a small amount of CO₂, as oxidant directly, and for a long time the alkaline fuel cell almost gave its way to proton exchange membrane fuel cell (PEMFC) which is also a kind of fuel cell being researched intensively in recent years [8]. However, the advantages with alkaline fuel cell are too attracting for researchers to give it up and in recent years alkaline fuel cell is being considered as one promising alternative to PEMFC [9, 10]. One of the advantages is that the alkaline fuel cell works under alkaline condition which is more favorable for the electrode reaction than acid condition, this makes it possible to cut or even avoid the use of noble metal as catalyst [8]. Another advantage is that the functional ionic OH⁻ is generated at the cathode and travels to the anode. This travel direction is in the reverse of that for fuel diffusion. As a result, in this way a reversed electro-osmotic effect is formed and the troublesome problem of fuel cross over for direct methane fuel cell (DMFC) may be resolved [11, 12]. What is more, water is generated at the anode in alkaline fuel cell, and this difference from PEMFC may provide a novel way to solve the water managing problem that is complex and can not be neglected [13]. Still another important advantage is that in alkaline environment, the catalyst is less likely to get poisoned [14]. This may provide a way for fuel cells to work with fuels other than pure hydrogen. This is important because the pure hydrogen is not likely to be available widely due to difficulties in produce, transport, storage and distribution [15]. With these advantages, the AFC may get popular if novel alkaline electrolyte can be explored to solve the CO₂ related issue. Thus, many efforts have been tried to explore novel electrolyte [16] alternative to the conventional KOH and NaOH.

While seeking for alternative alkaline electrolyte, a kind of basic salt of hydrogen phosphate (M₂HPO₄) was interested. These salts are alkaline, but seem unlikely to react with CO₂. Take K₂HPO₄ for example. When CO₂ reacts with K₂HPO₄, a salt of KH₂PO₄ shall be resulted via Eq. (1). However, the acidity of KH₂PO₄ is higher than that of H₂CO₃. As a result, the CO₂ shall be released and KH₂PO₄ shall be resulted again. Consequently, the KH₂PO₄ shall not react with the CO₂. Therefore, the M₂HPO₄ seems to be an interesting alkaline electrolyte for AFC and some related investigations were conducted as early as in 1960s [17]. However, no tests of the electrolyte were seen in a real single fuel cell, and no tests on CO₂ tolerance were carried out.



In this paper, the electrolyte of M₂HPO₄ was investigated as electrolyte for AFC by assembling a single fuel cell. The results show that a maximum power density of 60 mW cm⁻² was obtained. Tests also show that no significant decrease in performance was observed when CO₂ was introduced to the oxygen stream.

2. EXPERIMENTAL

2.1 Electrolyte preparation

Materials— K_2HPO_4 99% and Na_2HPO_4 99% were used as received. The two salts were dissolved in distilled water to obtain a saturated transparent solution as electrolyte. The pH was measured with test paper to be around 12.

2.2 Fuel cell test

A piece of filter paper (45 mm×45 mm×100 μm in size) was immersed in the electrolyte obtained above for 2 hours at room temperature, and a semi-transparent sample can be obtained. The filter paper was used for its considerable chemical stability, good mechanical property. More importantly, paper alone itself has been proved not to transport H^+ or OH^- . With this membrane carrying the electrolyte, it is easy to tell whether the electrolyte is functional or not.

Afterwards, the membrane was sandwiched between two pieces of catalysed carbon paper to obtain membrane electrode assembly (MEA). The Pt/C catalyst loading was 0.5 mg cm^{-2} , and the area is $2.5 \text{ cm} \times 2.5 \text{ cm}$. The MEA was subsequently clamped between two graphite blocks with serpentine flow channels for hydrogen and oxygen flow, and the cell was clamped between two stainless steel plates using a set of retaining bolts around the periphery of the cell. PTFE sheets were used on both sides of the MEA for isolation and sealing. Hydrogen and oxygen were supplied at a flow rate of 10 and 20 ml min^{-1} , respectively. Current and voltage were recorded with a multimeter (PLZ70UA, Japan) at room temperature.

Stability test was carried out while keeping the current density to be 100 mA cm^{-2} . Influence of CO_2 was investigated by injecting CO_2 with purity of 99% into the oxygen stream during the stability test.

The influence of electrolyte was investigated by injecting the electrolyte to the oxygen stream while keeping the current density at 140 mA cm^{-2} .

3. RESULTS AND DISCUSSION

3.1 Polarization test

The single cell test results at room temperature are presented in Fig. 1. The open circuit voltage (OCV) was observed to be 0.9 and 0.99 V for the fuel cell with Na_2HPO_4 and K_2HPO_4 , respectively. The value agrees with several reported values with other electrolytes [18, 19]. This means that both the electrolytes do not poison the catalyst. However, the OCV for the fuel cell with K_2HPO_4 is about 100 mV higher than that with Na_2HPO_4 . This implies that the K_2HPO_4 is superior to Na_2HPO_4 as electrolyte for the fuel cell.

The maximum current density at 0.2 V for K_2HPO_4 and Na_2HPO_4 was observed to be 95 and 170 mA cm^{-2} , further confirming that the superiority of K_2HPO_4 to Na_2HPO_4 .

The maximum power density (MPD) for the fuel cell with Na_2HPO_4 was observed to be around 30 mW cm^{-2} . However, that for the fuel cell with K_2HPO_4 was around 60 mW cm^{-2} . Although this value is not high [20], it reveals the promising possibility of the salts as electrolyte for AFC. The results mean that both hydrogen phosphate can work as electrolyte for fuel cell, and K_2HPO_4 seems to be more suitable since it offers higher fuel cell performance.

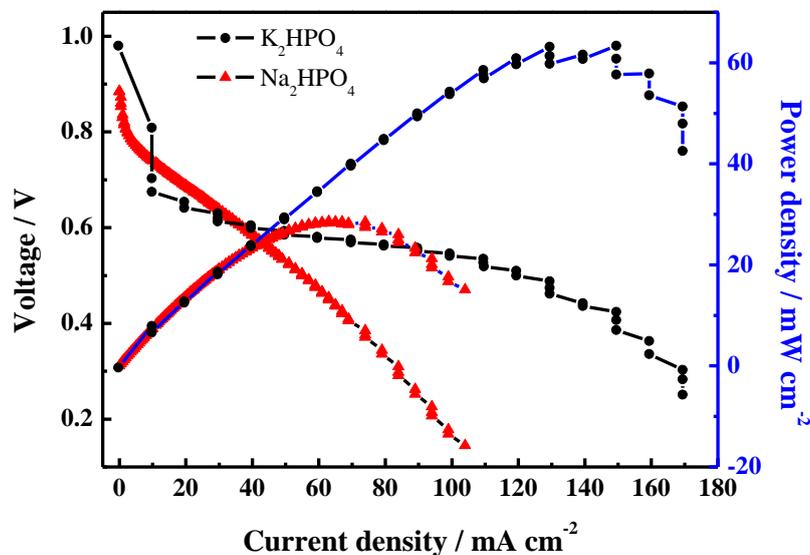


Figure 1. Polarization curves of fuel cells with the Na_2HPO_4 and K_2HPO_4 at room temperature

3.2 CO_2 tolerance

If alkaline fuel cell is tolerable to CO_2 , the fuel cell can then work with air free of scrubbing system. As a result, the structure of the fuel cell can be simplified and the price can be lowered. Therefore, CO_2 tolerance of the electrolyte is an important factor to value the alkaline electrolyte. Therefore, CO_2 was introduced to the fuel cell with K_2HPO_4 as electrolyte while keeping the current density at 100 mA cm^{-2} . The result is presented in Fig. 2(a). It can be seen that the voltage dropped from 1.0 V quickly to around 0.6 V. This agrees with the result presented in Fig. 1. The voltage can maintain at around 0.6 V for at least 3600s.

When CO_2 was introduced at 1800s, a slight decrease in voltage was observed in Fig. 2(a), as can be observed more clearly in Fig. 2(b). This decrease may be caused by the lack of oxygen when CO_2 was injected. However, the voltage recovered quickly as observed, and no acceleration of voltage reduction was observed. This means that the CO_2 did not jeopardize fuel cell performance by poisoning the electrolyte. However, when KOH was used as electrolyte, the fuel cell performance shall decrease progressively [21-24]. Therefore, it is reasonable to conclude that the K_2HPO_4 has reasonable tolerance to CO_2 . The results may pave a new way to develop alkaline electrolyte for fuel cell that is tolerable to CO_2 .

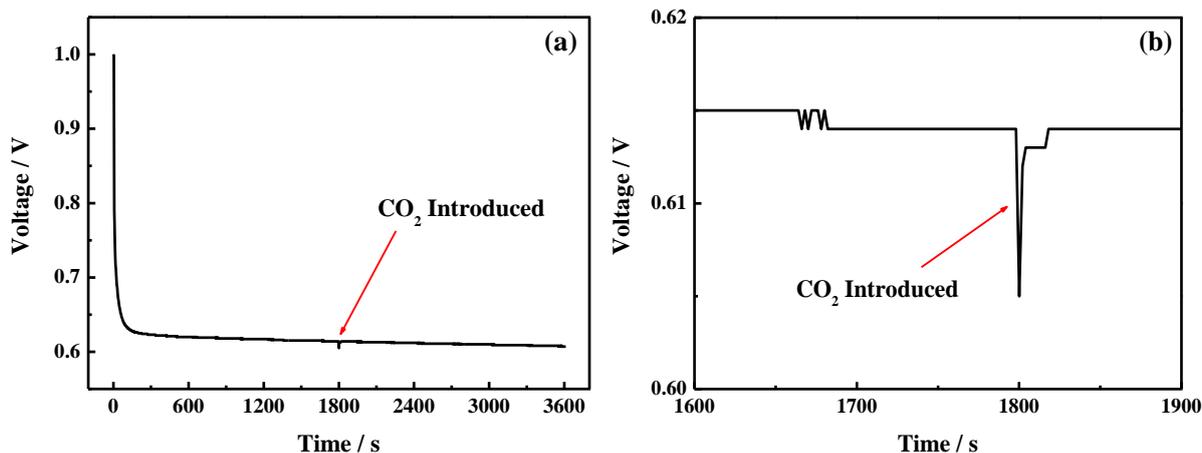


Figure 2. (a) Stability test with introduction of CO₂, (b) magnified figure of (a) at the time when CO₂ was introduced

3.3 Stability test

Stability test shown in Fig. 3 demonstrates that the voltage decreases with time. It is supposed that the decrease may be caused by the leaching of the electrolyte. Therefore, another test was conducted by injecting K₂HPO₄ electrolyte keeping the current density at 150 mA cm⁻² and the result is presented in Fig. 3. It can be seen that the voltage decreased with time. However, when the electrolyte was injected, as shown in Fig. 3 at 1800s, the voltage recovered to be higher than 0.4 V. When the injection was repeated, another recovery was observed. This means that the decrease is largely due to the leaching of electrolyte.

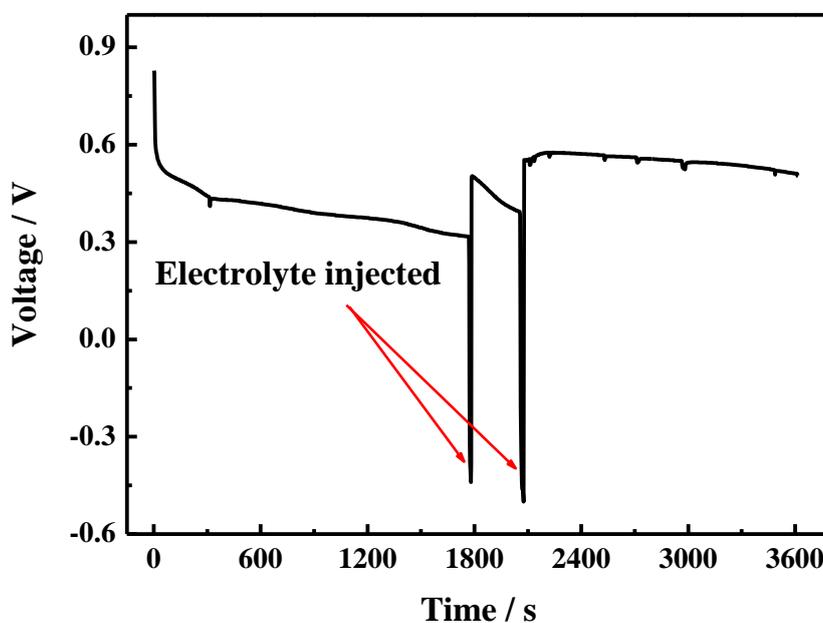


Figure 3. Stability test with introduction of K₂HPO₄

4. CONCLUSION

In conclusion, basic salt of hydrogen phosphate was investigated as electrolyte for AFC. A MPD of 60 mW cm^{-2} was obtained at 0.5 V with K_2HPO_4 . Stability tests show that the fuel cell can work for at least 3600s without significant decrease in performance. CO_2 tolerance tests show that no performance decrease happened obviously when the electrolyte was exposed to CO_2 . Although the fuel cell performance is still low, it shows the possibility of M_2HPO_4 to work as electrolyte for AFC. These results imply it may be an interesting way to develop alkaline electrolyte for AFC that can work with air containing some CO_2 .

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References

1. B. C. H. Steele and A. Heinzl, *Nature*, 414 (2001) 345.
2. L. J. J. Janssen, *Journal of Applied Electrochemistry*, 37 (2007) 1383.
3. M. Nogami, H. Matsushita, Y. Goto and T. Kasuga, *Advanced Materials*, 12 (2000) 1370.
4. M. A. Parrish, *Materials & Design*, 2 (1980) 68.
5. T. Fujigaya and N. Nakashima, *Advanced Materials*, 25 (2013) 1666.
6. H. Ye, J. Huang, J. J. Xu, N. K. A. C. Kodiweera, J. R. P. Jayakody and S. G. Greenbaum, *Journal of Power Sources*, 178 (2008) 651.
7. M. Galiński, A. Lewandowski and I. Stępnia, *Electrochimica Acta*, 51 (2006) 5567.
8. N. Wagner, M. Schulze and E. Gülzow, *Journal of Power Sources*, 127 (2004) 264.
9. N. W. Li, Y. J. Leng, M. A. Hickner and C. Y. Wang, *Journal of the American Chemical Society*, 135 (2013) 10124.
10. N. W. Li, T. Z. Yan, Z. Li, T. Thurn-Albrecht and W. H. Binder, *Energy & Environmental Science*, 5 (2012) 7888.
11. J. R. Varcoe and R. C. T. Slade, *Fuel Cells*, 5 (2005) 187.
12. H. Hou, G. Sun, R. He, B. Sun, W. Jin, H. Liu and Q. Xin, *International Journal of Hydrogen Energy*, 33 (2008) 7172.
13. M. B. Satterfield, P. W. Majsztrik, H. Ota, J. B. Benziger and A. B. Bocarsly, *Journal of Polymer Science Part B: Polymer Physics*, 44 (2006) 2327.
14. A. D. Modestov, M. R. Tarasevich, A. Y. Leykin and V. Y. Filimonov, *Journal of Power Sources*, 188 (2009) 502.
15. F. Vigier, S. Rousseau, C. Coutanceau, J. M. Leger and C. Lamy, *Topics in Catalysis*, 40 (2006) 111.
16. S. Suzuki and M. Nagai, *Materials Science and Engineering B: Advanced Functional Solid-State Materials*, 161 (2009) 138.
17. M. Beltzer, *Journal of the Electrochemical Society*, 114 (1967) 1200.
18. S. M. Haile, *Acta Materialia*, 51 (2003) 5981.
19. J. X. Wang, N. M. Markovic and R. R. Adzic, *Journal of Physical Chemistry B*, 108 (2004) 4127.
20. J. Gao, G. Wang, Z. W. Wang, Y. T. Wang, J. G. Liu, W. M. Liu and Z. G. Zou, *Journal of Materials Chemistry A*, 2 (2014) 19275.

21. L. H. Thaller, R. E. Post and R. W. Easter, *NASA Technical Memorandum*, X-52812 (1970) 1.
22. M. A. Al-Saleh, S. Gültekin, A. S. Al-Zakri and H. Celiker, *Journal of Applied Electrochemistry*, 24 (1994) 575.
23. P. D. Michael, *An assessment of the prospects for fuel cell powered cars*, ETSU, United Kingdom (2000).
24. G. F. McLean, T. Niet, S. Prince-Richard and N. Djilali, *International Journal of Hydrogen Energy*, 27 (2002) 507.

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