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# Carbonation effects on the performance of alkaline polymer electrolyte fuel cells

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## ABSTRACT

The carbonation effect on alkaline polymer electrolyte fuel cells (APEFCs) was investigated in the present work by the study of single-cell performance and electrochemical AC impedance. The carbonate anions in alkaline polymer electrolyte (APE) were found to lead to a decline in cell performance due to the increase in both the ionic resistance, in comparison to  $\text{OH}^-$  conduction, and the overall reaction resistance. When the  $\text{OH}^-$  in APE was partially or completely replaced with carbonate anions, through exposure to air or immersion in  $\text{KHCO}_3$  solution, respectively, the peak power density of  $\text{H}_2$ – $\text{O}_2$  APEFC single cell (operated at  $60^\circ\text{C}$ ) dropped from  $0.61\text{ W/cm}^2$  to  $0.47$  and  $0.43\text{ W/cm}^2$ , respectively. When air was used as the oxidant instead of pure  $\text{O}_2$ , the performance of APEFC single cell was further reduced because of the lower partial pressure of  $\text{O}_2$ ; the peak power density decreased to  $0.32\text{ W/cm}^2$ . If  $\text{CO}_2$  was removed from the air, the cell performance increased, to some degree, to  $0.41\text{ W/cm}^2$ . Whereas the influence of deliberate replacement of  $\text{OH}^-$  with carbonate anions in APE is rigid, the carbonation effect caused by air can be alleviated to a large degree by operating the cell under high current density, in which case enormous  $\text{OH}^-$  can be produced to refresh the APE and the electrode surface.

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## Introduction

Fuel cells have been recognized as a class of clean and efficient converter of energy, in particular for the hydrogen-based energy system [1,2]. Because of its compact structure, high power density, and capability of room-temperature startup, the polymer electrolyte fuel cells (PEFCs) have been considered as an ideal power source for vehicles and portable devices [3–5]. At present, although the proton exchange

membrane fuel cell (PEMFC) is the most advanced type of PEFCs, the polymer electrolyte, proton exchange membrane (PEM), is, however, a strong acid, which requires noble metal catalysts to be used as the catalysts for both the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR). This has been a major barrier to the widespread application of PEMFC [6,7].

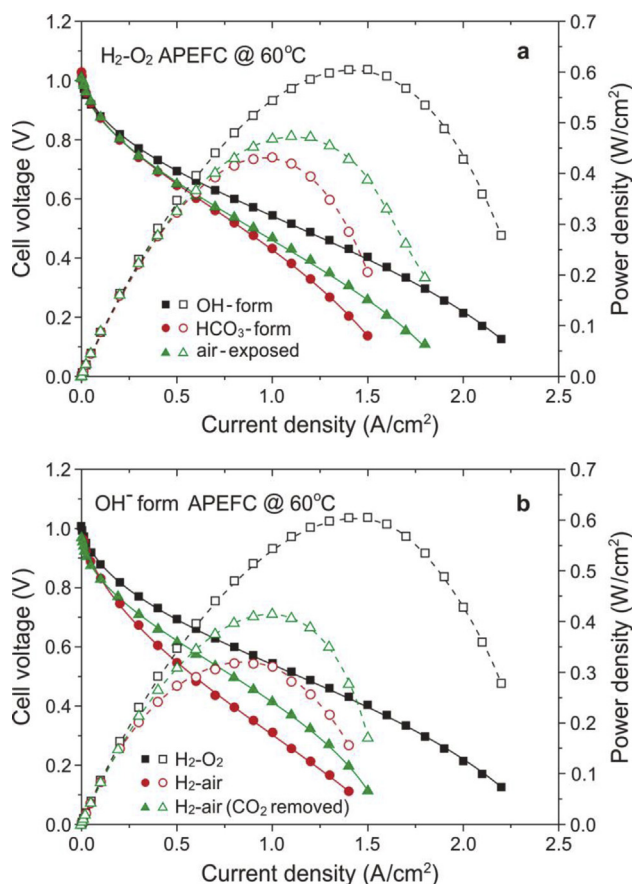
The alkaline polymer electrolyte fuel cell (APEFC) is a new type of PEFCs emerging in last decade. It is expected to combine the advantages of PEMFC and traditional alkaline

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**Fig. 1** – Cell performance of APEFCs operated at 60 °C with Pt/C catalyst. *a*QAPS-S<sub>8</sub> (IEC = 1.0 mmol/g) was used as both membrane (50 ± 5 μm in thickness) and ionomer solution (20 wt% in catalyst layer). Pt loading in both anode and cathode were 0.4 mg/cm<sup>2</sup>. (a) Comparison of APEFCs with different CCMs operated with pure H<sub>2</sub> and O<sub>2</sub> fed at a flow rate 150 mL/min and 100% humidified. (b) Comparison of APEFC with OH-form CCM operated with different oxidants. Air and CO<sub>2</sub>-removed air were fed at a flow rate of 300 mL/min and 90% humidified.

fuel cell (AFC), and nonprecious metal catalysts are therefore applicable in APEFC [7–14]. Furthermore, since the electrolyte is APE rather than concentrated KOH solution, the issue of carbonate precipitate, which would cause the electrolyte leakage of AFC, can be avoided [15,16].

Albeit no longer a fatal issue to fuel cell operation, the carbonation of APE is still a concern for the performance of APEFC. Previous studies have resulted in contradictory conclusions on this problem. Some researchers found the presence of carbonate species would not weaken the overall performance of APEFC [17,18]. Instead, the carbonate species in the fuel cell system seemed to have a beneficial effect on the ORR kinetics, and the carbonate anions (CO<sub>3</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup>) can improve the chemical stability of APE and thus benefit the long-time operation of APEFC [15,18]. In contrast, other researchers found unfavorable effects of carbonate on the performance of APEFC [19–22] not only because the carbonate anions have led

to a reduction in the ionic conductivity of APE [19,21], but also to an unfavorable impact on the HOR kinetics [23].

In principle, it should not be difficult to clarify this problem by looking at the change in cell performance upon carbonating the APE and/or switching the oxidant from O<sub>2</sub> to air. However, the cell performance of APEFC in aforementioned studies were quite low, probably due to the lack of high-performance APE in form of both membrane and ionomer in catalyst layer, thus the assessment of the carbonate effect on APEFC should have also been affected by other fuel cell operating conditions. Thanks to our recent development in high-performance APE based on self-aggregated quaternary ammonium polysulfone (*a*QAPS), the cell performance of APEFC has been improved significantly. Now we think it is time to re-examine the carbonation effects on the performance of APEFC. Our approach is to compare the performance of APEFC single cells using APEs in OH-form or carbonate-form, and also to look at the effect of replacing O<sub>2</sub> with air for fuel cell operation. Electrochemical AC impedance is applied in the present work to investigate the influence in reaction kinetics.

## Experimental

### Materials

All the materials used for the synthesis of self-aggregated quaternary ammonium polysulfone (*a*QAPS-S<sub>8</sub>) were the same as reported in our previous studies [24]. 60wt% Pt/C was purchased from Johnson Matthey Co.. Potassium hydroxide (Sinopharm Chemical Reagent Co. Ltd., 85%) and potassium carbonate (Sinopharm Chemical Reagent Co. Ltd., 99%) were used as received. The preparation of *a*QAPS-S<sub>8</sub> membrane and ionomer solution have been reported in detail in our previous paper [24].

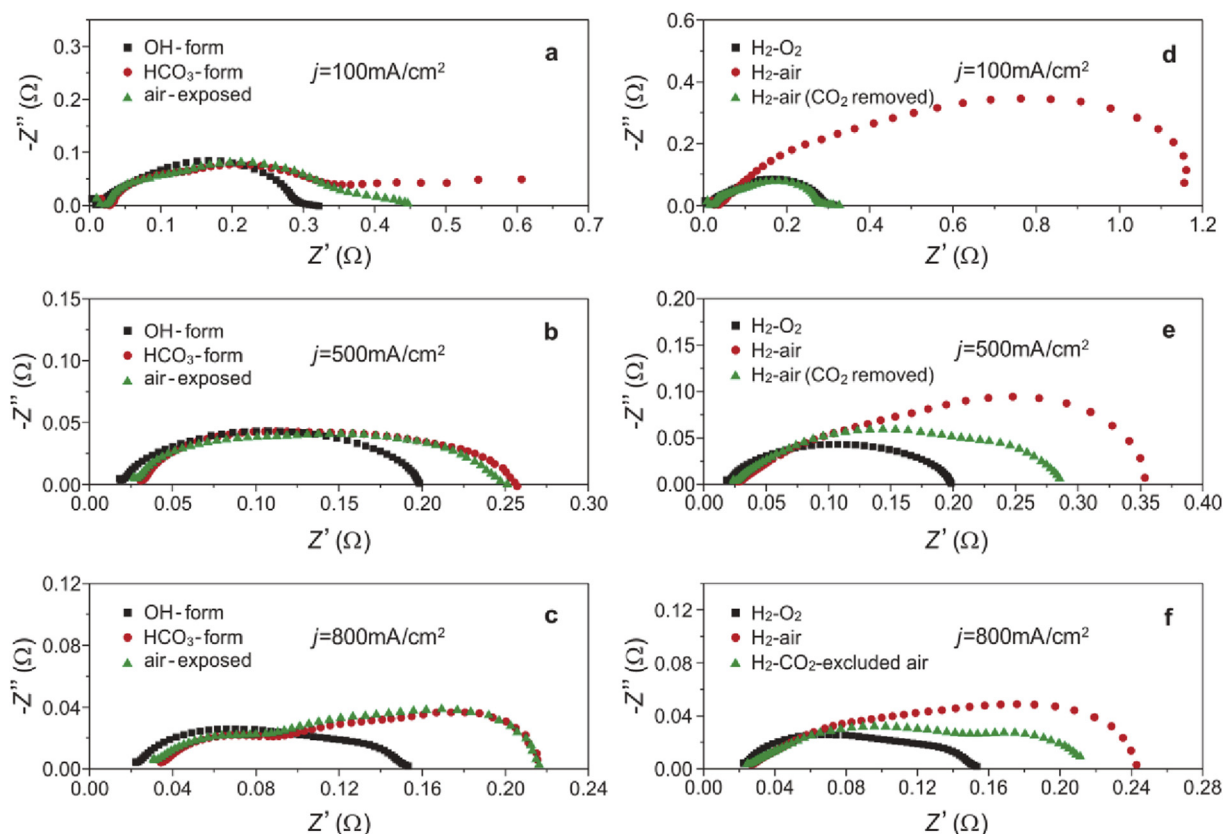
### Preparation of membrane-electrode assembly

Pt/C catalyst was mixed with certain amount of self-aggregated quaternary ammonium polysulfone (*a*QAPS-S<sub>8</sub> in Cl<sup>-</sup> form) ionomer solution, which was then sprayed onto each side of an *a*QAPS-S<sub>8</sub> (in Cl<sup>-</sup> form) membrane (50 ± 5 μm in thickness) to produce the catalyst-coated membrane (CCM). The Pt loading in both anode and cathode was controlled to be 0.4 mg/cm<sup>2</sup>, and the area of the electrodes was 4 cm<sup>2</sup>. The weight percentage of *a*QAPS-S<sub>8</sub> ionomer in both the anode and the cathode was calculated to be 20wt%.

To study the carbonation effect of APEFC, three typical CCMs had been prepared. By immersing the CCM in 1 mol/L KOH and 1 mol/L KHCO<sub>3</sub> solution for 24 h at room temperature, OH- and HCO<sub>3</sub>-form CCMs were achieved. Subsequently, by exposing the OH-form CCM in air for 7 days at room temperature, the air-exposed CCM was obtained. The CCMs were sandwiched between two pieces of carbon paper (AvCarb GDS3250) to make the membrane electrode assembly (MEA).

### Fuel cell tests

Different types of fuel cell were tested using a fuel-cell test station (850e Multi Range, Scribner Associates Co.) in a



**Fig. 2** – Nyquist plots of AC impedance results for APEFCs tested at 60 °C under different current densities, 0.1, 0.5, and 0.8 A/cm<sup>2</sup>. For (a), (b) and (c), the fuel cells were assembled with different forms of CCM, and operated with pure H<sub>2</sub> and O<sub>2</sub>. For (d), (e), and (f), the fuel cells were assembled with OH-form CCM and operated with different oxidants.

galvanic mode at 60 °C with a backpressure 0.1 MPa on both sides. All of the APEFCs were operated under their optimized conditions. For H<sub>2</sub>–O<sub>2</sub> APEFC, the cell was operated with fully humidified (100% relative humidity (RH)) H<sub>2</sub> and O<sub>2</sub> gases flowing at a rate of 150 mL/min. For H<sub>2</sub>–air and H<sub>2</sub>–air (CO<sub>2</sub> removed) APEFCs, fully humidified H<sub>2</sub> was supplied in anode with a flow rate (FR) of 150 mL/min, while the FR and RH of (CO<sub>2</sub> removed) air in cathode were 300 mL/min and 90%, respectively.

AC impedance data were collected under current densities of 0.1, 0.5, and 0.8 A/cm<sup>2</sup>, superimposed by an AC current with 5% amplitude of the DC current, using Scribner Associates 880 Frequency Response Analyzer. The testing frequency range was set from 0.1 Hz to 10 kHz. The high-frequency resistance ( $R_{hf}$ ) was used directly to monitor the ionic conduction, while the distance between the  $R_{hf}$  and the low-frequency resistance (the right-hand interception on the real axis of impedance) was taken as an approximate index of the overall reaction resistance ( $R_{rxn}$ ).

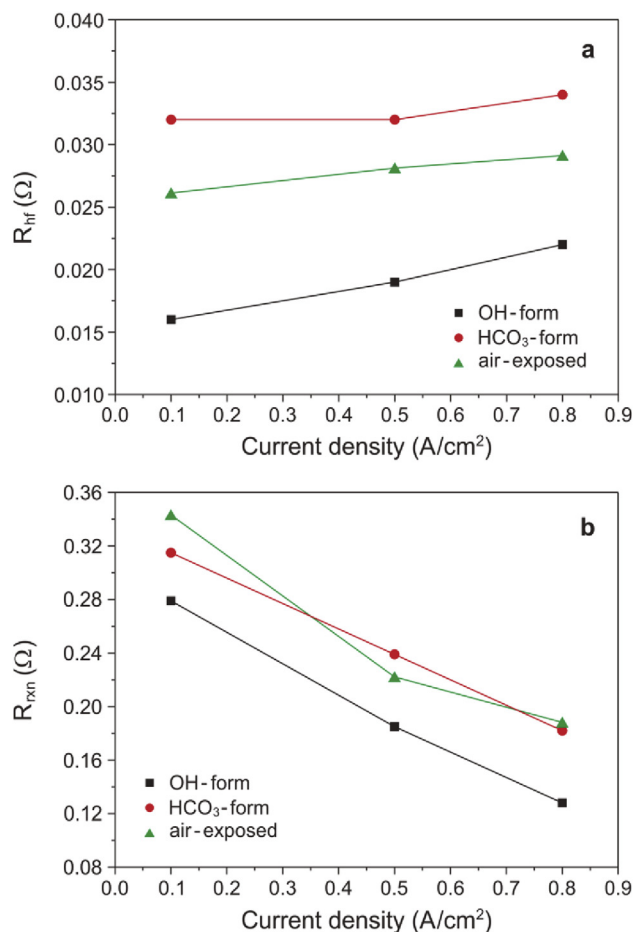
## Results and discussion

In the present work, carbonate species were introduced into the APEFC system in two fashions: One is to replace the anion

in APE with carbonate anions (CO<sub>3</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup>), and the other is to use air instead of O<sub>2</sub> as the oxidant for fuel cell test.

### Effects of carbonate anions in APE on the performance of H<sub>2</sub>–O<sub>2</sub> APEFC

In the catalyst-coated membrane (CCM), the APE acts as both the membrane and the binder of catalyst powder. Ideally, all anions of APE in CCM are expected to be OH<sup>-</sup>. However, during the fuel cell assembly, the CCM is unavoidable to be exposed to air. For different techniques of fuel cell assembly, the carbonation degree in CCM would be different. In order to study the impact of carbonate anions in APE on the APEFC performance, we deliberately leaved an OH-form CCM in air at room temperature for 7 days (marked as air-exposed CCM). As shown in Fig. 1, when the fuel cell was operated with pure H<sub>2</sub> and O<sub>2</sub>, the performance of the air-exposed CCM was notably lower than that of the pristine OH-form CCM (which may have been slightly carbonated though). The peak power density of the air-exposed CCM was 0.47 W/cm<sup>2</sup> at 60 °C under a current density of 1.1 A/cm<sup>2</sup>, which was 21.8% lower than that of the OH-form CCM (0.61 W/cm<sup>2</sup>) at a current density of 1.5 A/cm<sup>2</sup>. To further study the effect of carbonate anions in APE, another CCM, whose anions were completely replaced with bicarbonate ions (HCO<sub>3</sub><sup>-</sup>), was tested. It seemed that the completely

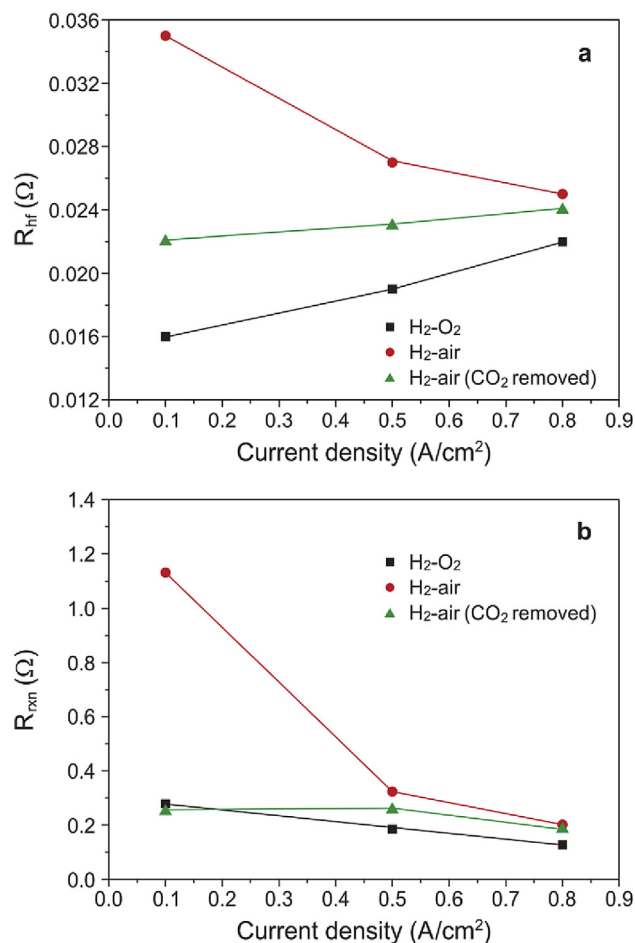


**Fig. 3** – High-frequency resistance ( $R_{hf}$ , a) and overall reaction resistance ( $R_{rxn}$ , b) extracted from AC impedance data in Fig. 2a–c, showing the carbonation effects caused by carbonate anions deliberately introduced into APE before fuel cell operation.

carbonated CCM gave a further reduction in cell performance (Fig. 1), the peak power density was  $0.43 \text{ W/cm}^2$  under a current density of  $1.0 \text{ A/cm}^2$ , which was lower than that of the air-exposed CCM, and 28.8% lower than that of the OH-form CCM.

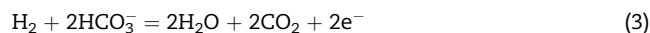
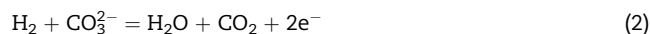
AC impedance analysis was employed to study the effects caused by carbonate anions in APE on the cell performance. The high-frequency resistance ( $R_{hf}$ ) and the overall reaction resistance ( $R_{rxn}$ ) were extracted from the Nyquist plots (Fig. 2). Fig. 3 compares the  $R_{hf}$  and the  $R_{rxn}$  in H<sub>2</sub>–O<sub>2</sub> APEFCs with different anions. The  $R_{hf}$  (Fig. 3a) of the air-exposed CCM was 1.3–1.6 times higher than that of the OH-form CCM, and when the anion in the CCM was entirely HCO<sub>3</sub><sup>–</sup>, the  $R_{hf}$  increased further, giving a 1.6 to 2.0 times larger value in comparison to that of the OH-form CCM. The increase in  $R_{hf}$  upon carbonation was mainly due to the lowered ionic conductivity in APEs (the ionic conductivity of APE with OH<sup>–</sup> was about 3.8 times higher than that of the APE with carbonate anion) [21].

When the CCM was operated under a specific current density, a certain amount of OH<sup>–</sup> was generated at the cathode by the ORR, which then migrated across the membrane to the anode side. Therefore, for the carbonated APEFC, all of the



**Fig. 4** – High-frequency resistance ( $R_{hf}$ , a) and overall reaction resistance ( $R_{rxn}$ , b) extracted from AC impedance data in Fig. 2d–f, showing the carbonation effects caused by CO<sub>2</sub> in air.

anions, including OH<sup>–</sup>, CO<sub>3</sub><sup>2–</sup>, and HCO<sub>3</sub><sup>–</sup>, would react with H<sub>2</sub> and produce H<sub>2</sub>O and CO<sub>2</sub> (Eqs. (1)–(3)).



In principle, the thus-produced CO<sub>2</sub> can be removed by the flowing H<sub>2</sub> in anode and the carbonate anions in the CCM can be gradually refreshed back to OH<sup>–</sup>, leading to a reduction in  $R_{hf}$ . Such self-purging process, however, was not observed during the limited period of operation in the present work.

Fig. 3b displays the difference of  $R_{rxn}$  between the carbonated and the OH-form CCMs. There was no obvious disparity in  $R_{rxn}$  between air-exposed and the completely carbonated CCMs, but both of them show values 1.1 to 1.5 times higher than that of the OH-form CCM. The increase of  $R_{rxn}$  in



carbonated APEFCs should be due to the change in the overpotential of electrochemical reactions. In the cathode, since the ORR produces  $\text{OH}^-$  in APEFC, the high pH can be maintained, the overpotential of ORR should not be sensitive to the existence of carbonate anions. However, in the anode, the enrichment of carbonate anions could result in a reduction of pH, leading to an increase in the overpotential of HOR.

### Carbonation effects in $\text{H}_2$ -air APEFC

Applying air as the oxidant for APEFC is another way to introduce carbonate species into the CCM. As demonstrated in Fig. 1b, for the OH-form CCM, when air was supplied, the peak power density decreased to  $0.32 \text{ W/cm}^2$  at  $60^\circ\text{C}$ , in comparison to  $0.61 \text{ W/cm}^2$  in the case of pure  $\text{O}_2$ . However, it's worth noting that the trace  $\text{CO}_2$  existing in air is not the only reason for the performance drop, the lower partial pressure of  $\text{O}_2$  in air should have also cast some influence. To identify how the  $\text{O}_2$  concentration affects the fuel cell performance,  $\text{CO}_2$  was removed from the air (marked as  $\text{CO}_2$ -removed air) and supplied to the cathode. The resulting peak power density was  $0.41 \text{ W/cm}^2$ , 31.6% lower than that of pure  $\text{O}_2$  supplied APEFC.

Fig. 4a illustrates the difference of  $R_{\text{hf}}$  between cells operated with  $\text{CO}_2$ -removed air and with pure  $\text{O}_2$ . Although there was no carbonate species in the fuel cell system, the  $R_{\text{hf}}$  still increased to some degree when  $\text{CO}_2$ -removed air was supplied, which may be due to the relatively lower RH applied in this case. Fig. 4b compares the difference in  $R_{\text{rxn}}$ . At low current density, the low partial pressure of  $\text{O}_2$  caused almost no difference in  $R_{\text{rxn}}$ ; while at high current density, the ORR kinetics was obviously affected by the insufficient  $\text{O}_2$  supply, the  $R_{\text{rxn}}$  for  $\text{CO}_2$ -removed air increased to a value of 1.6 and 1.7 times higher than that of pure  $\text{O}_2$ . Therefore, to promote the  $\text{O}_2$  supply in the cathode, the air should be fed with a higher flow rate. With a gas flow rate (FR) of  $0.3 \text{ L/min}$ , the peak power density for  $\text{CO}_2$ -removed air supply can reach  $0.41 \text{ W/cm}^2$  at  $60^\circ\text{C}$  under a current density of  $1.0 \text{ A/cm}^2$ .

With the knowledge for operating APEFC with  $\text{CO}_2$ -removed air, we tested the  $\text{H}_2$ -air APEFC under the optimized FR and RH conditions. As shown in Fig. 4a, the  $R_{\text{hf}}$  increased notably in particular under low current density. This should be due to the contamination effect of  $\text{CO}_2$  to the APE. While at high current density,  $\text{OH}^-$  was enormously produced by the ORR, the carbonation effect on APE became less and less, showing a decreasing dependence of  $R_{\text{hf}}$  on the current density, which is clearly different from that without  $\text{CO}_2$ . At a current density as high as  $0.8 \text{ A/cm}^2$ , the  $R_{\text{hf}}$  for the  $\text{H}_2$ -air APEFC fell to a level close to that of  $\text{CO}_2$  removal, suggesting that although the  $\text{CO}_2$  in air can contaminate the APE and reduce the ionic conductivity, the APE can be refreshed by applying high current density.

As for the  $R_{\text{rxn}}$  of  $\text{H}_2$ -air APEFC (Fig. 4b), the increase in  $R_{\text{rxn}}$  is obvious at low current density, in comparison to APEFC operated with  $\text{O}_2$  or  $\text{CO}_2$ -removed air; but at high current density, the  $R_{\text{rxn}}$  was almost identical to that for  $\text{CO}_2$ -removed air. This should be once again an effect caused by the enormous production of  $\text{OH}^-$  in cathode under high current density. In other words, the carbonation effect caused by  $\text{CO}_2$  in air is negligible when an APEFC is operated under high current density.

## Conclusions

By replacing the  $\text{OH}^-$  in CCM with carbonate anions, the cell performance of APEFC will decrease to a notable degree. The effects of carbonate anions in CCM include the lowering in ionic conductivity and restraining the electrode reactions in particular the HOR. Therefore, in practice, the as-prepared OH-form CCM should be carefully treated during fuel cell assembly so as to avoid carbonation.

When an APEFC with OH-form CCM is operated with air instead of  $\text{O}_2$ , the cell performance will drop due to the lower partial pressure of oxygen and the  $\text{CO}_2$  contamination. The carbonation effect caused by air, however, can be alleviated to a large degree by operating the cell under high current density, in which case enormous  $\text{OH}^-$  can be produced to refresh the APE and the electrode surface.

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