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In situ microobservation of the cathode in molten carbonate fuel cells

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Abstract

In molten carbonate fuel cells (MCFC), the wettability of the electrode and the electrolyte distribution are very important factors influencing the active reaction area. We have observed the molten carbonate behaviour directly on the cathode (porous NiO) and the electrolyte plate ($LiAlO_2$) under various gas conditions and at controlled potentials using an environmental scanning electron microscope (ESEM) equipped with a hot stage. We estimated the liquid electrolyte distribution in the cathode and measured the contact angles on NiO and $LiAlO_2$ in the electrolyte. Moreover, the electrolyte movement in the reaction $CO_2 + \frac{1}{2} O_2 + 2\,e^- = CO_3^{2-}$ was observed on the surface of the porous NiO in a CO_2/O_2 atmosphere. The reaction $CO_3^{2-} + 2\,e^- = CO + 2\,O^{2-}$ of the gas generation was observed in a H_2O atmosphere. The active reaction points on the electrode are the areas where the electrolyte film is thin.

1. Introduction

High-power density of molten carbonate fuel cells (MCFC) can be attained by increasing the active reaction area on the electrode. The active reaction area is closely related to the electrolyte distribution. If the active reaction points can be identified, it is possible to design the electrode to increase the generating power density. Electrolyte distribution depends on (i) the wettability of the electrodes, (ii) the pore size distribution of the electrode, and (iii) the capillary force balance in the anode/electrolyte plate/cathode system.

In previous work we presented an electrolyte distribution model, which took account of the electrode wetting property and the pore size distribution within the electrode. Using this model and the wetting property data, the electrolyte distribution in the electrode was calculated for various MCFC operating conditions [1, 2]. This model is effective on a macro-level, but cannot determine the electrolyte distribution on a micro-level. So far the microstructure has been observed with a solidified electrolyte.

In this study we observed the molten carbonate behaviour directly on the cathode (porous NiO) and the electrolyte plate ($LiAlO_2$) under various gas conditions and at controlled potentials using an environmental scanning electron microscope (ESEM) equipped with a hot stage. We have discussed the relation between the electrode and the electrolyte, and the active reaction points.

2. Experimental details

2.1. *Microscopic experimental device*

Figure 1 shows an outline of the experimental device, which observes the molten carbonate behaviour on the electrode on a micro level. This device is chiefly composed of an environmental scanning electron microscope (ESEM) (Nikon, model ESEM-2700), an energy dispersive X-ray spectroscopy (EDS) (Noran Instruments, model D-6217), and a potentiostat–galvanostat (Solartron, model 1287). A heating stage was installed in the sample room of the ESEM, and it was possible to achieve a temperature of 1000 °C. ESEM and SEM are similar, but the principle of the electron signal detection is different. Thus ESEM can observe the sample without electroconductive treatment, under high pressure (SEM:1×10^{-3} Pa, ESEM:$10 \sim 2700$ Pa) and various gas conditions [3, 4].

2.2. *Electrochemical cell*

Figure 2 shows a schematic diagram of the electrochemical cell. The working electrode is porous NiO whereas the counter electrode is a gold crucible (inside dia.: 7 mm, height: 1 mm). The reference electrode is a Au mesh. A carbonate mixture $[(Li_{0.53}Na_{0.47})_2CO_3]$ is used as the electrolyte. The electrolyte plate is $LiAlO_2$.

The basic operating conditions are: Temperature 480–650 °C, pressure 200 Pa. The supplied gases are mixtures of H_2O, CO_2, N_2, O_2 and air.

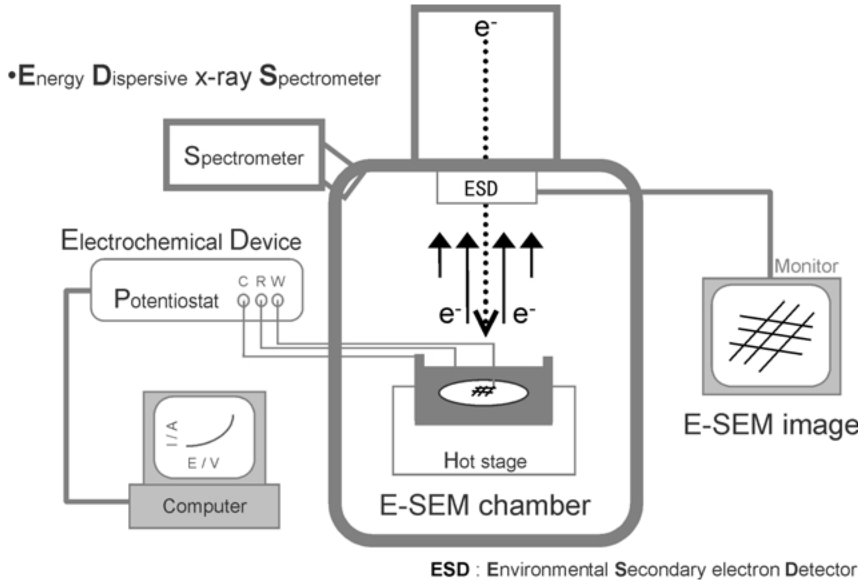


Fig. 1. Schematic illustration of experimental apparatus.

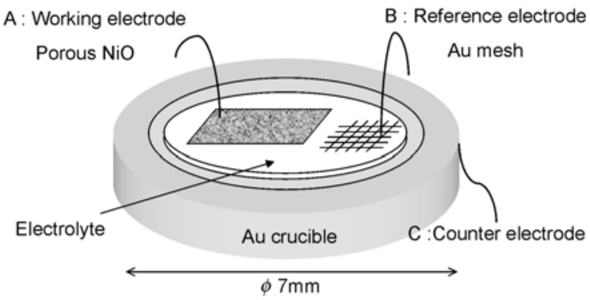


Fig. 2. Schematic diagram of electrochemical cell.

2.3. *Preparation of porous NiO*

The oxidization process of Ni was described previously [5]. A porous Ni plate (25 mm × 25 mm × 0.9 mm) was partially immersed in molten carbonate, oxidized and lithiated in CO_2/O_2(=66/33%). After the oxidization process, the immersion of NiO continued for 200 h, and the crystallization of NiO particles was promoted.

2.4. *Determination of the contact angle*

The method used for the determination of the contact angle was the sessile-drop method. The schematic principle is shown in Figure 3. The substrates were crystallized NiO particles and a single crystal of $LiAlO_2$ (Crystal GmbH).

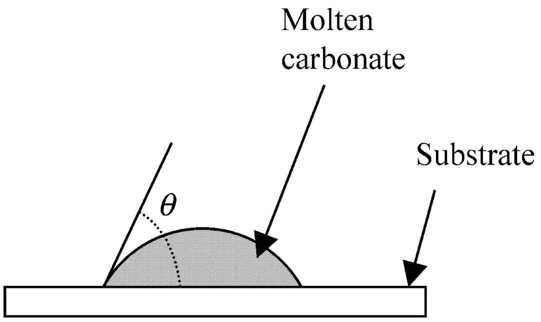


Fig. 3. Schematic principle of sessile-drop method.

3. Results and discussion

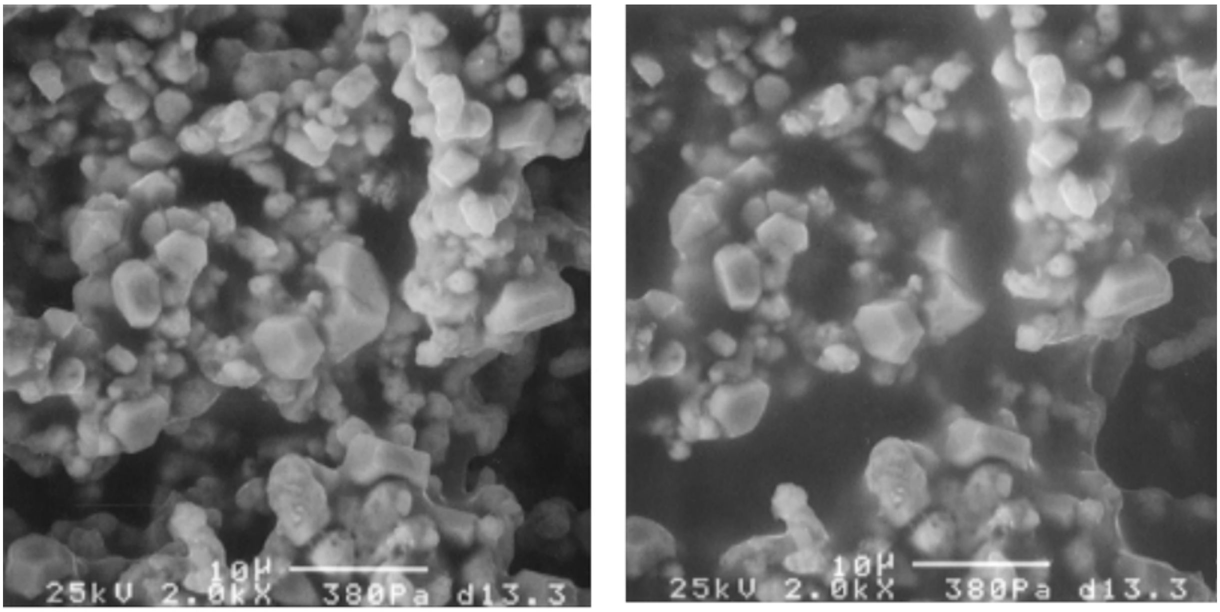
3.1. *Electrolyte distribution in a solid and liquid state*

Figure 4 shows the comparison between the solidified electrolyte distribution and the liquid electrolyte distribution. Regarding the secondary electron intensity, the colour of the NiO particles is whitish and the colour of the electrolyte darkish. As the electrolyte film on the NiO thickens, the colour becomes blacker. In the solid state, the amount of electrolyte seen on the surface of the electrode is small, and the NiO particles can be observed clearly; in the liquid state, the electrolyte soaks into the surface of the electrode, and the NiO particles in the interior cannot be seen in the electrolyte. It is easier to observe the inner NiO particles in the solid state than in the liquid state. The different electrolyte distributions are caused as follows. (i) The volume is different in the electrolyte state. (ii) The electrolyte gathers at the place where the electrolyte previously coagulated, because the wettability of the coagulated electrolyte in the liquid electrolyte is good. (iii) During the electrolyte coagulation process, the empty hole becomes smaller due to the coagulated electrolyte causing the electrolyte to move further towards the empty hole by means of capillary force.

3.2. *Wettability of electrode and electrolyte plate in electrolyte*

3.2.1. *Wettability of NiO in electrolyte*

It is known that the cathode overvoltage, which is the main factor determining MCFC performance, is mainly



(a) Solid (temperature: about 480°C) (b) Liquid (temperature: about 530°C)

Fig. 4. Microscopic image showing the surface of a porous NiO in CO_2.

controlled by the distribution of the electrolyte in the cathode. However, there is hardly any data regarding the contact angle of the cathode (NiO) in the electrolyte. Because NiO is very wet and it is not easy to obtain a smooth surface, the generation of the electrolyte droplets and therefore the measurement of the contact angle of the cathode is very difficult. Hence, the contact angle of the cathode in the electrolyte has so far been assumed to be zero, and the electrolyte distribution was calculated in previous work [1,2].

Recently, Suski et al. discussed the wettability of NiO single crystals and the NiO deposited on a Au substrate by ion sputtering [6, 7]. The difference between the contact angle on the NiO-deposit layer and the NiO single crystal in the Li/Na carbonate is about 10°. Therefore, it is necessary to measure the contact angle on the lithiated NiO.

It is known that a part of the NiO particles, which has been operating as a MCFC cathode for a long time, is easy to crystallize, as shown in the center of Figure 4. The droplets of the carbonate can be observed on a comparatively large surface of the NiO particle as shown in Figure 5, and the contact angle on the NiO in the electrolyte was measured by using the sessile-drop method. The contact angles of NiO depend on the gas composition. Figure 6 shows the effect of the CO_2 concentration on contact angle; the higher the CO_2 concentration, the larger the contact angle.

When the contact angle is close to 10°, it is easy for the droplets to break and spread. Moreover, the contact angle on a different face of the crystal has a different value. These discrepancies lead to the experimental scatter shown in Figure 6.

Figure 7 shows the effect of temperature on the contact angle in a CO_2 atmosphere. The contact angle appears to become smaller, the higher the temperature. Within the measured range, the contact angle is assumed to be nearly proportional to temperature. The curve describing the relationship has an inclination of −0.06 °C. This temperature dependence of NiO is smaller than that of Ni. This value is about 1/8 of the temperature dependence of the anode Ni [1].

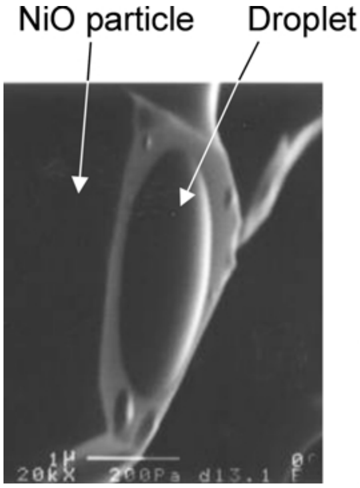


Fig. 5. Microscopic image of molten carbonate droplet on NiO in 67% CO_2 and 33% O_2 atmosphere.

In addition, the influence of the potential was examined between 0.0 V and −0.3 V (vs o.c.p.). Although the effect the potential has on the contact angle could not be observed, as shown in Figure 8, because the measured range of potential is narrow (since NiO is reduced, the measurement range cannot be extended), we were not able to distinguish between the effect the potential has

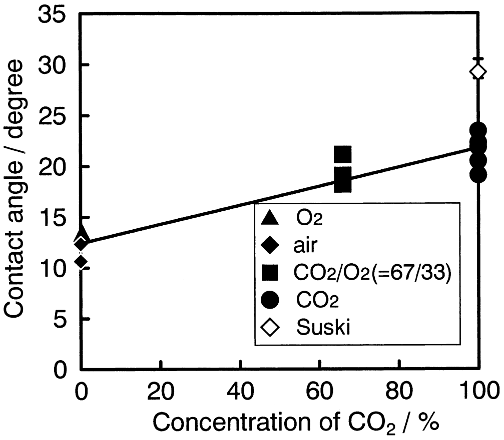


Fig. 6. Effect of CO_2 concentration on contact angle.

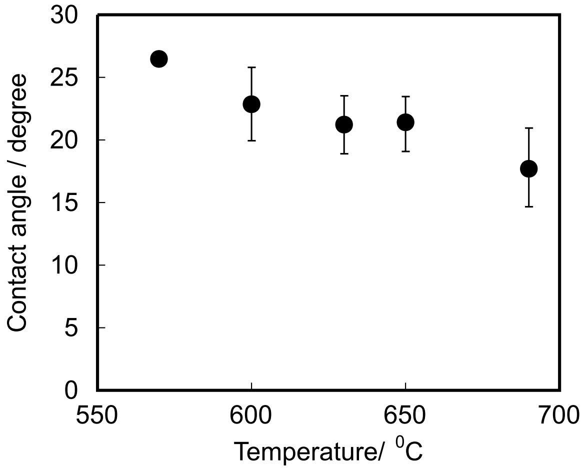


Fig. 7. Effect of temperature on NiO wetting characteristic in CO_2.

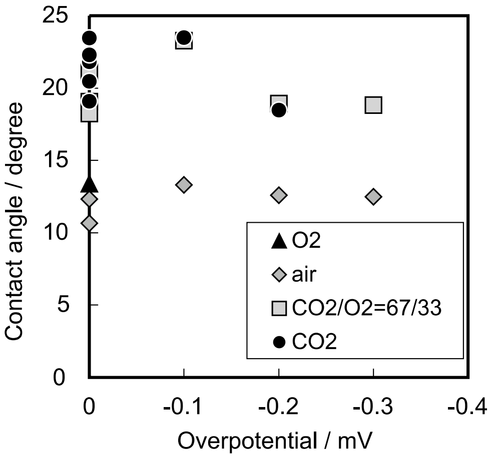


Fig. 8. Effect of overpotential on contact angle.

and experimental errors. Therefore, the effect of potential on the contact angle is negligible compared with the effect of other factors.

We have compared the present results with Suski et al. [6] and found that there is a small difference between the contact angle of the *in situ* oxidized NiO and the NiO single crystal at 650 °C. The difference is about 8° in a 100% CO_2 atmosphere. However, the measurement pressure differs greatly between 200 Pa and 101 325 Pa (1 atm) in the experiments of Suski et al., although the effect of the pressure is very slight.

3.2.2. *Wettability of $LiAlO_2$ in electrolyte*

A porous $LiAlO_2$ plate is generally used as the electrolyte plate in MCFCs. So far the wettability of $LiAlO_2$ has hardly been discussed. The reason for this is that the mean pore size in the electrolyte plate is 1/10 smaller than that in the anode and cathode, and that the electrolyte plate is normally filled with the electrolyte. Therefore, the effect of $LiAlO_2$ wettability on electrolyte distribution is negligible compared with that of other components. However, the pore size of $LiAlO_2$ becomes larger with operating time, the capillary force of the electrolyte plate becomes lower, and the electrolyte loss increases. It is therefore necessary to establish the wetting property data for $LiAlO_2$ to determine the maximum pore diameter that must be maintained by the electrolyte in the electrolyte plate.

The contact angle measurements were carried out on $LiAlO_2$ as well as on NiO. Figure 9 shows the effect of gas composition on contact angle. The contact angle of $LiAlO_2$ appears to become smaller, the higher the CO_2 concentration. This dependence is the same as that of NiO. Figure 10 shows the effect of temperature in a CO_2 atmosphere. The contact angle is assumed to be nearly proportional to temperature; the curve describing the relationship is −0.06 °C and therefore nearly equal to that of NiO.

3.2.3. *Comparison of the contact angles on NiO, $LiAlO_2$ and Ni*

Figure 11 shows a comparison between the contact angles on NiO, $LiAlO_2$ and Ni in a CO_2 atmosphere. The data for Ni was obtained by using the vertical-plate measurement in a reducing ($H_2/CO_2/H_2O$) atmosphere [1]. The wetting of $LiAlO_2$ is better than that of NiO. The dependence of the CO_2 concentration can also be seen in Ni.

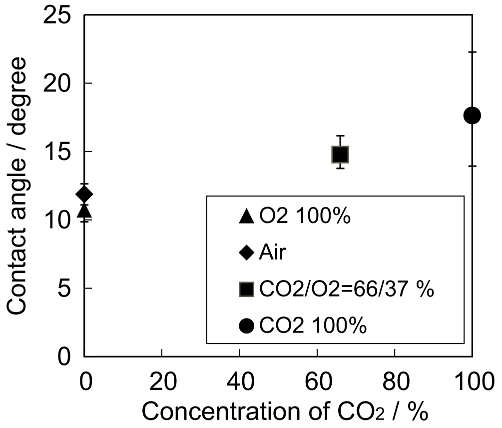


Fig. 9. Effect of CO_2 concentration on $LiAlO_2$ single-crystal wetting characteristic.

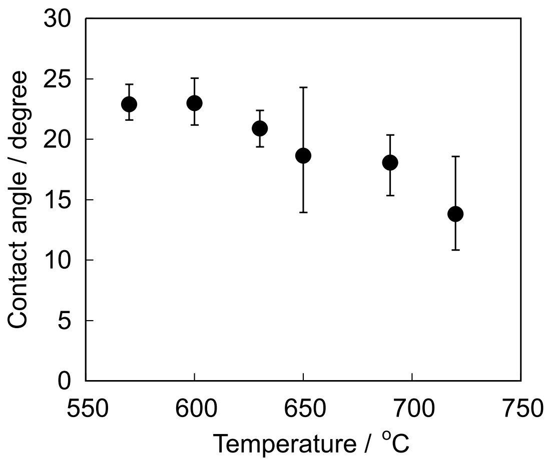


Fig. 10. Effect of temperature on $LiAlO_2$ single-crystal wetting characteristic in CO_2.

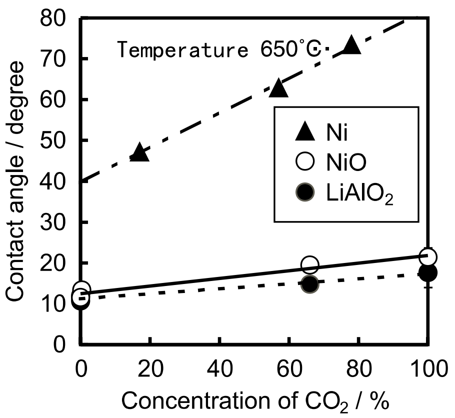


Fig. 11. Comparison of contact angle on NiO, $LiAlO_2$ and Ni in CO_2.

3.3. *Electrolyte behaviour in the MCFC cathode reaction*

The effect of potential on the relation between the electrode and the electrolyte was examined to determine the active reaction points. In our previous work [8], the super meniscus of the electrolyte covered the Au mesh electrode if the potential sweep was performed in a negative direction in a $N_2/CO_2/O_2$ atmosphere. The thickness of the supermeniscus was found to be approximately 0.1 to 0.5 μm. In this work, we have observed the behavior of the electrolyte on NiO as well as on Au.

In Reaction 1, the growth of the electrolyte droplets in a CO_2/O_2 atmosphere is observed on the crystallized NiO particles:

$$CO_2 + \frac{1}{2} O_2 + 2\,e^- = CO_3^{2-} \tag{1}$$

Figure 12 shows the appearing and disappearing electrolyte droplet at −0.3 V (vs o.c.p.) and 650 °C. In

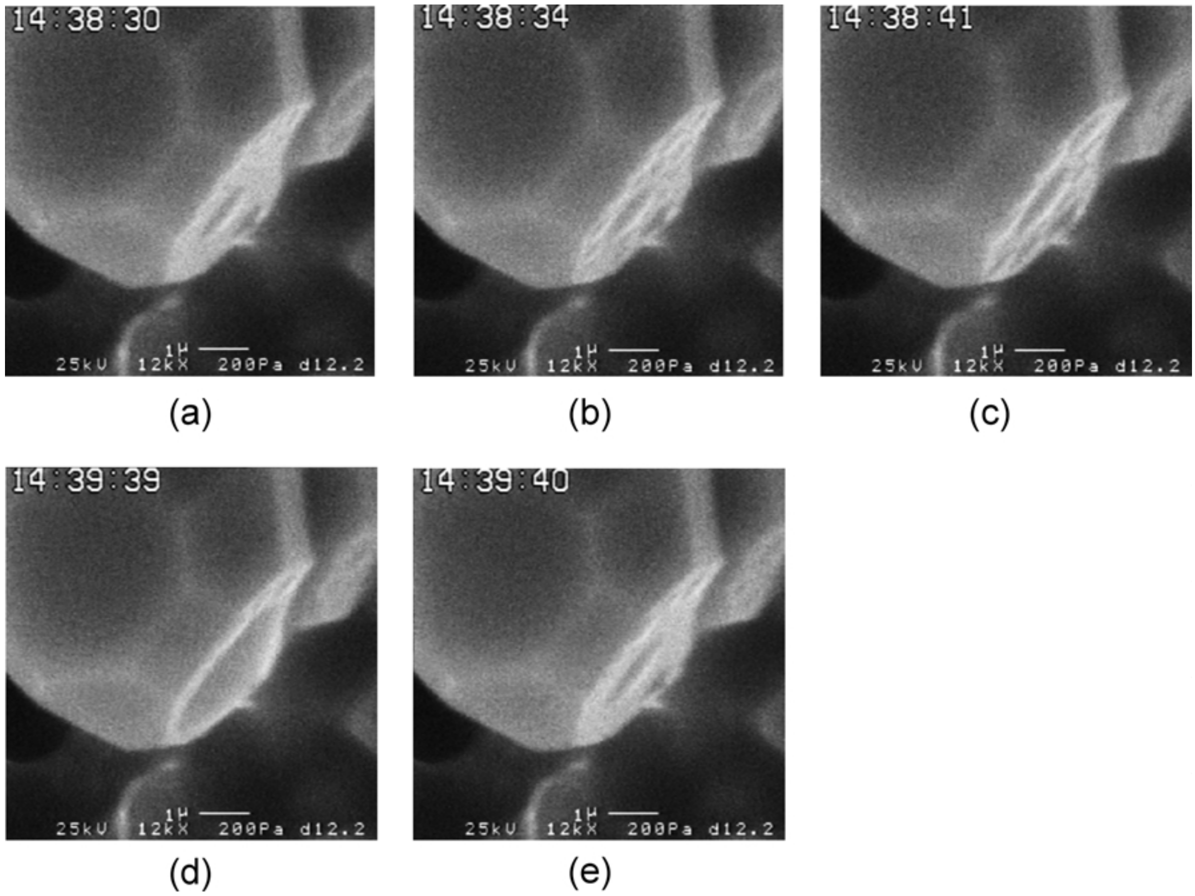


Fig. 12. Movement of electrolyte droplets in the reaction $CO_2 + \frac{1}{2} O_2 + 2\,e^- = CO_3^{2-}$ on the surface of the porous NiO. Potential, −0.3 V (vs o.c.p.); temperature 650 °C; pressure, 200 Pa; gas composition, CO_2/O_2=66/33.

Table 1. Average Ni$K\alpha$/Na$K\alpha$ peak ratio on surfaces where droplets appear and do not appear

Surface	Ni$K\alpha$/Na$K\alpha$ peak ratio
Droplets appear	180–240
Droplets do not appear	100–150

Figure 12(a), one medium-sized droplet and some small droplets can be seen. After 4 s, in Figure 12(b), the small droplet has become larger and new small droplets have appeared. After a further 7 s, in Figure 12(c), the droplets have grown and some droplets have joined to make larger droplets. After a further 58 seconds, in Figure 12(d), most droplets have joined together and become a lot larger. After a further 1 s, in Figure 12(e), the largest droplet has been destroyed and appears to be flat. Once again small droplets have been generated. The growth of the electrolyte droplets becomes faster, the higher the overpotential. Also, the height of the droplets is about 0.1–0.5 μm, and a change in brightness around the droplets is observed. This change is caused by the moving electrolyte film, which seems to be the super meniscus. However, it is not possible to measure the thickness of the electrolyte film, which is extremely thin. The result of these images is that the appearance of the droplet will show the generation of the carbonate, and that the positive ion (Li^+, Na^+) will be transported through the super meniscus.

On the surface where the droplets do not appear, a change in the electrolyte behaviour in Reaction 1 is not observed. To compare the thickness of the electrolyte film, the peak intensities of Na$K\alpha$ and Ni$K\alpha$ are measured on many surfaces by EDS. Table 1 lists the average Ni$K\alpha$/Na$K\alpha$ peak ratio on the surfaces where the droplets appear and do not appear. Because this peak ratio is low for surfaces where droplets do not appear, the electrolyte film on these surfaces is thicker than the height of the droplet.

3.4. *Active reaction point on the electrode*

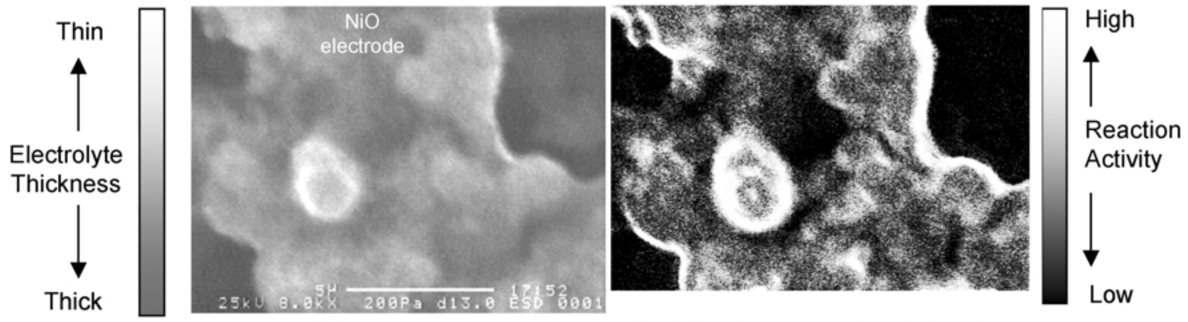
It is possible to observe the generation of the electrolyte droplet in the cathode reaction of MCFCs on some of the surfaces of NiO particles. It is not possible to observe movement on the surfaces where droplets do not appear. Thus, there is no way of understanding the active cathode reaction points. However, when the potential is set at -0.7 V (vs o.c.p.) in a H_2O atmosphere, the reaction with gas generation is observed on the surface of the porous NiO electrode. That reaction is

$$CO_3^{2-} + 2\,e^- = CO + 2\,O^{2-} \tag{2}$$

The process of gas generation was recorded on video, and the change in brightness, which had become visible due to the gas generation, was analyzed. The method of analysis used was to integrate the changes in brightness per unit area and unit time, and draw a diagram of the average changes per unit time. Figure 13 shows one video picture frame and the analysed map.

In Figure 13(b), the concentration of colour shows the changed activity, or the reaction activity of the gas generation. It shows that the reaction is active in the areas where the colour is whitish. In Figure 13(a), the color is whiter, the thinner the electrolyte film on the NiO electrode. Figure 13(a) and (b) show that the place where the electrolyte film is comparatively thin corresponds to an active reaction point. Therefore the gas generation activity depends on the electrolyte film thickness. If the active reaction points in Reaction 1 are nearly equal to those of Reaction 2, the part of the thinner electrolyte film should be increased to achieve a high performance MCFC.

For example, the following method may be used. When a MCFC operates for a long time, the crystallinity of the NiO particles increases. Therefore a cathode is composed of the NiO particles which are highly crystalline from the very beginning in order to decrease the surface roughness of the NiO particles. Furthermore, the following method has been determined: The substance, which is less wetted by electrolyte than NiO, is arranged amongst NiO particles, which cause part of the electrode to have a repelling effect on the electrolyte. Due to this method, the area, which was covered by electrolyte and rarely contributed to the reaction, is activated.



(a) Image (b) Active reaction Po int

Fig. 13. The position of gas generation on the surface of a porous NiO electrode in H_2O. Temperature 650 °C; pressure, 200 Pa; gas composition, H_2O=100%.

4. Conclusion

The *in situ* observation of MCFC cathodes in an ESEM gives information about the wettability of NiO and $LiAlO_2$, the electrolyte distribution and the active reaction point.

(i) We have observed electrolyte behaviour directly on the cathode. The electrolyte distribution in the electrode depends on the state of the electrolyte (solid or liquid) and the gas composition. The wetting properties of NiO and $LiAlO_2$ are improved if the electrolyte has a lower CO_2 concentration.

(ii) The generation of carbonate in a CO_2/O_2 atmosphere was observed on the surface of porous NiO.

(iii) Presently, the active reaction point in Reaction 1 is not clear. However, the active points in Reaction 2 correspond to the thinner part of electrolyte film on NiO. If the active reaction points in Reaction 1 are nearly equal to those in Reaction 2, the part of the thinner electrolyte film should be increased to achieve a high performance MCFC.

The results show that the structure of the electrode must be designed to take account of the changes in electrolyte distribution, which depends on the gas composition and the state of the electrolyte.

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