Mechanism of Electrowetting of Molten Carbonate

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Introduction

Electrode reactions of a molten carbonate fuel cell (MCFC) take place in three-phase contact line or a submerged reaction zone. For this reason, its performance is greatly influenced by the microscopic place for electrode reaction (reaction area and thickness of molten carbonate determined by the wettability) formed on the electrode wetting in molten carbonate. It is very important to understand a microscopic electrode-reaction place correctly toward the development and advancement of MCFC. That is, it can be reflected when producing long-life cell and highly efficient cell by stabilizing and controlling the reaction place. Therefore, in order to understand the electrode reaction place, a microscopic mechanism, which the molten carbonate gets wet for the electrode reaction (applied voltage), needs to be cleared. However, such a mechanism has been hardly understood from the optical observation under the operation conditions of MCFC until now.

In this study, so as to explain a microscopic wetting mechanism for the molten carbonate, the relation of the contact angle and the applied voltage to the electrode of a molten carbonate is clarified using the environmental control type electron microscope (E-SEM) which can carry out in-situ observation of electrode and molten carbonate at high temperature.

Experimental

We have attempted to observe the in-situ microscopic wetting behavior using environmental scanning electron microscope [1, 2] (ESEM : Nicon, model ESEM-2700) attached with hot stage in chamber and electrochemical device (Solartron, model 1287). ESEM can observe a sample without electroconductive treatment, under a high pressure and under various gas conditions. On the ceramic heating stage of the ESEM chamber, Au crucible (ϕ7 [mm], a depth of 2 [mm]) was constituted as a counter electrode, the electrolyte plate ($LiAlO_2$) which made carbonate (Li_2CO_2 / Na_2CO_3 = 53 / 47) impregnate beforehand in it was installed, and an inert electrode (Au mesh) as a working electrode and a reference electrode (Au mesh) were set on it. Thus, the prepared sample surface was directly observed using by ESEM. The method used for the determination of a contact angle is the sessile-drop method.

Result and discussion

When an applied voltage increased under CO_2 (trace O_2) gas at 923 [K] and 200 [Pa], the contact angle of the molten carbonate and the inert electrode (Au) became small as same as macroscopic optical observation [3](fig. 1). As a result, the interface area with the electrode containing the electrode-reaction place spread. In order to explain this phenomenon, so-called "electrowetting", we applied an electrical-double-layer model of Helmholtz to the distribution of a charge on the electrode surface. From this, it proved that change of the contact angle applied voltage originates in increase of an electrostatic energy accumulated at the interface of the electrode and the molten carbonate from the related formula of the contact angle and the applied voltage as following (fig.2).

$$\cos\theta(\mathrm{V}) = \cos\theta(\mathrm{V}_0) + \frac{1}{2}\frac{C'}{\gamma_{gl}}(\mathrm{V} - \mathrm{V}_0)^2 \quad (1)$$

Although this model was a considerably rough approximation near the electrode, it was simulating the change of contact angle well. Moreover, a double layer capacity obtained from the upper formula from parameter C' is 45 [μF/cm^2], and was well in agreement with the value acquired indirectly, 80-100 [μF/cm^2] [4]. Furthermore, the upper formula has given the ratio (A/*l*) of the area and thickness of the electrical-double-layer, and brought about the geometric information on the electrode surface.

Conclusion

The so-called "electrowetting" phenomenon that the molten carbonate was covered and spreaded by the applied voltage was clarified, using ESEM. Moreover, the electrowetting mechanism of the molten carbonate was clarified by deriving the formula to the applied voltage of the contact angle by applying the electric double layer model of Helmholtz to the distribution of the electric charge on the electrode interface.

References

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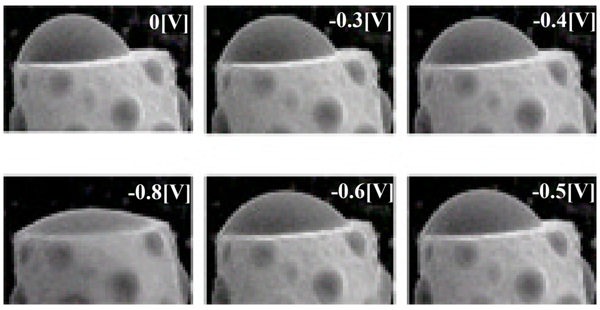

Fig.1 ESEM images of droplet of molten carbonate on the inert electrode during applying voltage under CO_2 (trace O_2) at 923 [K] and 200 [Pa].

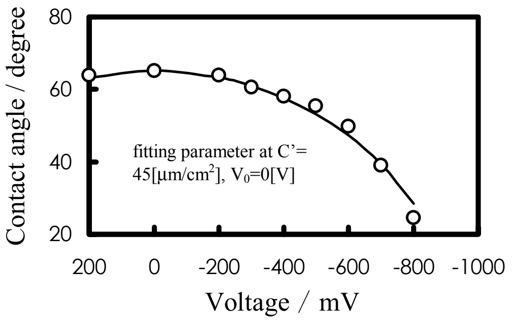

Fig.2 The contact angle between molten carbonate and inert electrode as a function of applied dc potential under CO_2 (trace O_2) at 923 [K] and 200 [Pa].