

Fabrication and characteristics of anode as an electrolyte reservoir for molten carbonate fuel cell

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Abstract

In order to design the anode of a molten carbonate fuel cell (MCFC) to serve as an additional electrolyte reservoir, the surface of a conventional Ni-10 wt.% Cr anode is modified with bohemite sol by means of a dip-coating method. After coating the bohemite sol on the nickel surface, the surface layer is changed into lithium aluminate particles during the course of cell operation. This results in good electrolyte wettability compared with a bare nickel surface. Consequently, the surface modification makes it possible to increase the electrolyte filling contents in the anode pores from 25–30 to 50–60 vol.%. In addition, the anti-sintering ability is induced due to the presence of lithium aluminate particles between the nickel particles. These findings show that the surface modification can increase both the structural stability and the electrolyte loading of the anode.

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Keywords: Molten carbonate fuel cell; Anode; Surface modification; Sol–gel coating; Wettability; Electrolyte reservoir; Structural stability

1. Introduction

A key technology for future power generation is the fuel cell, for which hydrogen is the best fuel. A fuel cell transforms chemical energy directly into electrical energy, and this generation is more efficient and environmentally benign. Advances in components and reduction in costs have to be made, however, before fuel cells can penetrate commercial markets [1].

There are many obstacles confronting commercialization of the molten carbonate fuel cell (MCFC), namely: overcoming NiO dissolution at the cathode [2]; corrosion [3,4], creep [5] and sintering of the anode; matrix cracking and electrolyte loss [5–7]. In particular, it is necessary to solve the problem of electrolyte loss, which causes a serious decay in performance, to achieve long-term operation of the MCFC. According to Hoffmann [8], electrolyte loss can be caused by various factors, e.g., corrosion of components [3], creepage [6], reaction with cell

components and direct evaporation [6,7,9]. These factors result in poor electrolyte–electrode contact, a small electrochemical reaction area, high ohmic resistance, gas cross-over, and gas leaking [9]. Excessive injection of electrolyte into a cell is not an effective remedy for electrolyte loss because the cell performance will be rapidly reduced by cathode flooding that inhibits the electrochemical reaction at the triple-phase boundary where fuel gas, liquid electrolyte and electrode meet. On account of the poor electrolyte wettability on the anode compared with the electrolyte-philic nature of the cathode, the electrolyte distribution is easily localized on the latter electrode. Even though Tanimoto et al. [10] reported successful long-term operation of single-cell through the addition of carbonate electrolyte during cell operation, it is very difficult to apply this method to a practical MCFC stack.

The study reported here discloses a new method for the injection of electrolyte into MCFCs without cathode flooding. This is achieved by modifying the surface properties of the anode to enable good wettability with electrolyte, as shown in Fig. 1. Specifically, bohemite sol is used as a coating material to provide an electrolyte reservoir. The operation of a cell with excessive electrolyte addition is examined.

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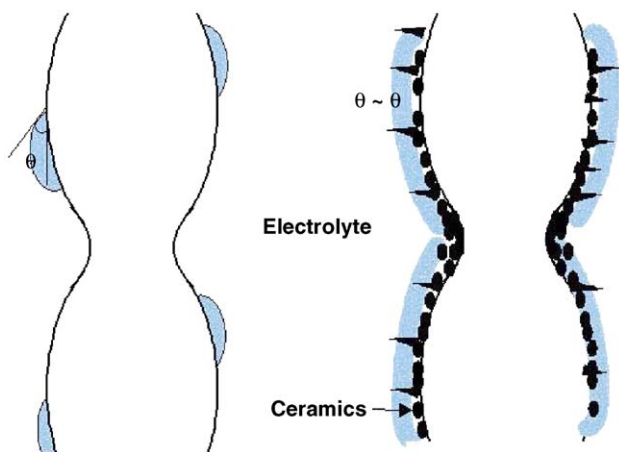


Fig. 1. Surface modification of nickel anode by sol-gel coating.

2. Experimental

2.1. Preparation of modified anode

A Ni-10 wt.% Cr anode was fabricated by tape casting. The green-sheet was sintered under a reducing atmosphere for 30 min at 1000 °C. The physical properties of the anode were: thickness = 0.7 mm; pore-size 3–4 μm; porosity 55–60%; specific surface area 0.1–0.2 m² g⁻¹ (Fig. 2).

An amount of 1 and 1.5 M bohemite sols were prepared from aluminum tri-sec-butoxide (ALTSB, 97%, ACROS) as ceramic coating materials. The anode was dip-coated into the bohemite sol for tens of seconds and dried at 120 °C in an oven for a day. After drying, the modified anode was calcined under a

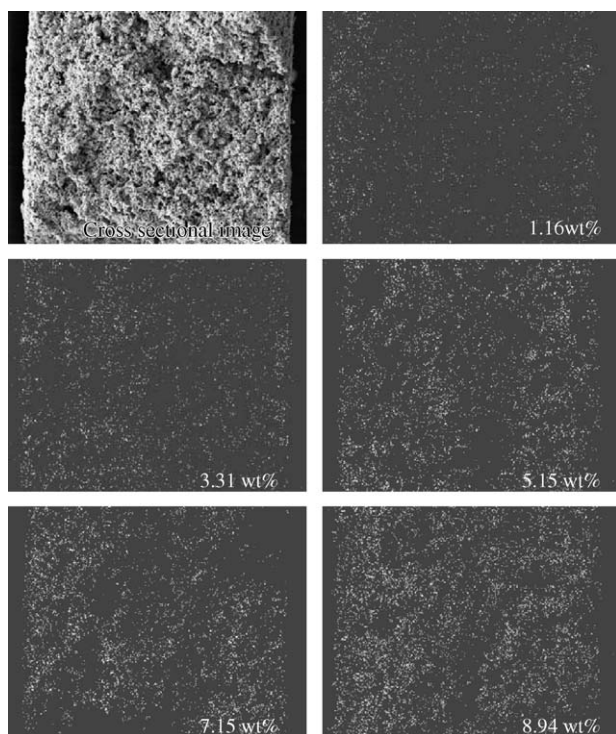


Fig. 2. Cross-sectional images of aluminium in anode after sol-gel coating.

nitrogen atmosphere for 6 h at 450 °C. The surface morphology of the modified anode was examined by means of scanning electro microscopy (SEM, Philips, FEI XL-30 FEG). In order to investigate the coating properties inside the anode, the distribution of aluminium was identified by cross-sectional mapping with an energy dispersive spectrometer (EDS). The phase changes due to the in situ reaction between the coating film and the electrolyte were analyzed by X-ray diffraction (Rigaku, D/MAX-2500). The porosity and pore-size of each sample were measured using the Archimedes method (ASTM C373–88) and a mercury porosimeter (AutoPore IV, Micromeritics), respectively.

2.2. Contact angle measurement

An improvement in anode wettability was identified by measurement of the contact angle with water. Because of difficulty in measuring the contact angle on a porous sample, however, the method of Lundblad and Bergman [11] was employed, namely, the use of the Washburn equation [12] to calculate the contact angle from capillary rise. In this procedure, modified anodes with various coating ratios (0–7 wt.% of anode weight) were mounted in a sample holder that was connected to a balance (SHIMADZU, AX 200) via a tungsten wire. The tip of the anode was placed over an alumina crucible that was fitted with water. The weight gain from the capillary rise of the anodes was monitored at room temperature in an air atmosphere.

2.3. Post-analysis after single-cell test

Cells with an active area of 10 cm × 10 cm were operated in a mixture of H₂:CO₂:H₂O = 72:18:10 as the fuel and air:CO₂ = 67:33 as the oxidant. The cells consisted of: (i) a γ-LiAlO₂ matrix with a porosity of 56%, a mean pore-size of 0.2 μm and a thickness of 2 mm; (ii) an anode coated with bohemite sol at a given coating ratio; (iii) a Li-doped-NiO cathode with a porosity of around 70%; (iv) an electrolyte of a 62 mol% Li₂CO₃ and 38 mol% K₂CO₃ eutectic. Measurements of nitrogen cross-over were conducted at the anode outlet by means of a gas chromatograph analyzer (HP 5890 series II). The cell performance, internal resistance (IR) and impedance spectra were measured with a Solartron 1260, frequency analyzer and a 1287, electrochemical interface. Electrochemical impedance spectroscopy (EIS) was performed with an excitation voltage of 10 mV in the frequency range of 10 kHz–10 mHz in order to analyze any changes in electrode polarization. After operation of the cells, the electrolyte contents in the components (anode, cathode, matrix) were analyzed by atomic absorption spectroscopy (AAS) and the inductively coupled plasma (ICP) method to assess the electrolyte distribution. Another method for analysis of the electrolyte contents was direct comparison of the difference in mass before and after electrolyte extraction. A 10% solution of acetic acid was used for extraction of the electrolyte in the cathode and the matrix. For the anode, however, de-ionized water had to be used in order to prevent nickel dissolution in the acid solvent.

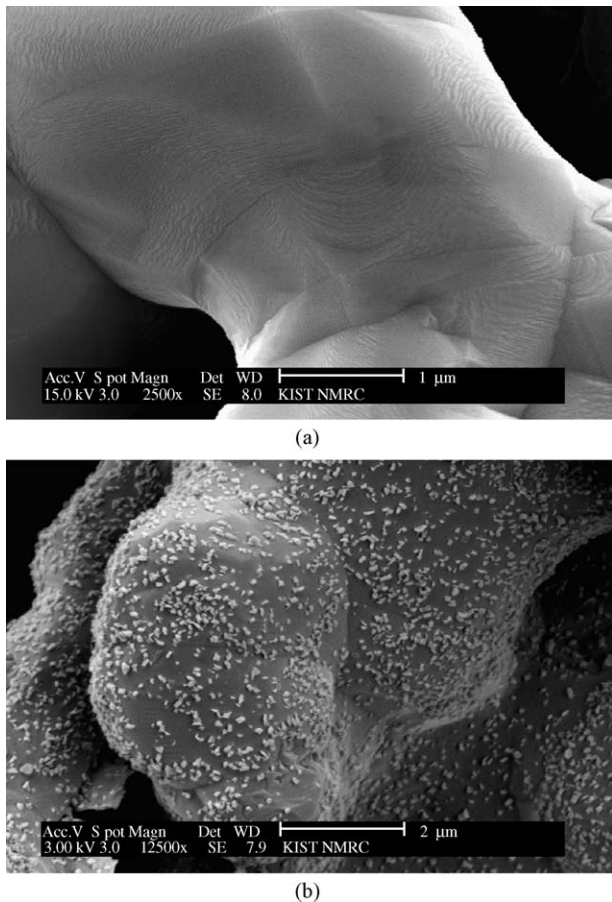


Fig. 3. Nickel surface (a) before coating and (b) after coating.

3. Results and discussion

3.1. Microstructure control by sol–gel coating

The weight gains of the anodes dip-coated with bohemite sol are directly proportional to the sol concentration and its coating times. The aluminium concentration (as determined by the EDS) shows that the coatings were uniformly applied throughout the pores of the anodes. After calcination, small particles of aluminum oxide are well-distributed on the nickel surface (Fig. 3(b)). It is clear, however, that the nickel surface is not entirely covered with the coating film, and this may increase the internal resistance.

In order to examine changes in the morphology of the coating film during cell operation, the alumina xerogel were immersed in the electrolyte eutectic under anode conditions. The XRD pattern for the xerogel reacted with the electrolyte is shown in Fig. 4 and is found to contain diffraction peaks for alpha (α -) and gamma (γ -) phase lithium aluminates, which have good stability during the operation of MCFCs. The small alumina particles (Fig. 3(b)) are changed into gamma lithium aluminate with a flaky form and alpha lithium aluminate with a spherical form, as shown in Fig. 5. From these observations of the surface morphology of the modified anode, it is concluded that the wettability can be increased by both improvement in the contact angle and in the roughness of the coated surface. The porosity of the anode

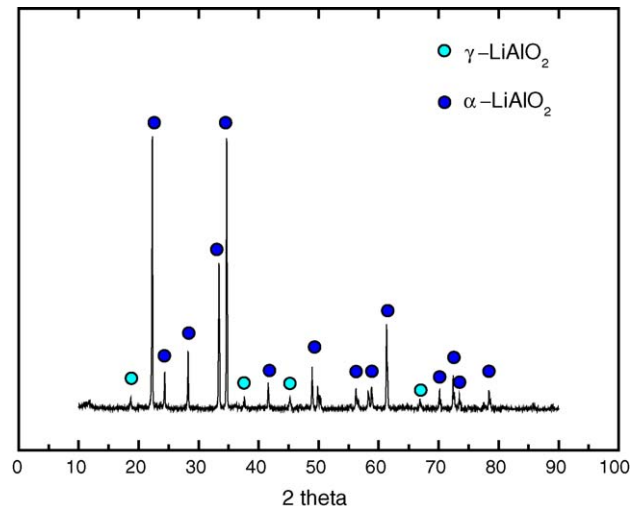


Fig. 4. XRD patterns of alumina xerogels reacted with Li/K electrolyte eutectic in a reducing atmosphere.

appears not to be controlled to any appreciable extent by the sol–gel coating (cf. Figs. 3 and 5). Therefore, in order to increase the quantity of electrolyte in the anode, both the pore-size and the contact angle of the anode are important. Because of the difficulty in measuring the contact angle on the porous anode, however, weight gains of the anodes in water were measured at room temperature as a function of the coating amount. The contact angle (calculated by the Washburn equation) decreases with increase in the coating amount, as shown in Fig. 6. From the results, it is concluded that the sol–gel coating can increase the wettability even in a practical application.

In order to determine the optimum coating ratio, the electrolyte filling contents were examined by the ICP/AAS method in under anode conditions. The filling contents continuously increase with increase in the coating amount (Fig. 7) as is expected from the increase in wettability shown in Fig. 6. The coating amount was optimized at around 5 wt.-%- Al_2O_3 on the anode because at greater amounts the internal resistance could be significant through overspreading with the resistive oxide particles.

3.2. Single-cell tests

The physical properties of the components and the amount of additional electrolyte used in the cell tests are summarized in Table 1. In order to compare the ability for electrolyte storage, three types of single-cells were operated. These cells had: (i) a standard anode with a normal amount of electrolyte; (ii) a standard anode with excessive amount of electrolyte; (iii) a modified anode with excessive amount of electrolyte. During cell testing, analyses of the oxygen gain and measurements of current–voltage (I – V) characteristics and impedance spectra were performed.

3.2.1. Oxygen gain test

Oxygen gain is the voltage difference when oxygen is substituted with an equivalent flow rate of air at the cathode.

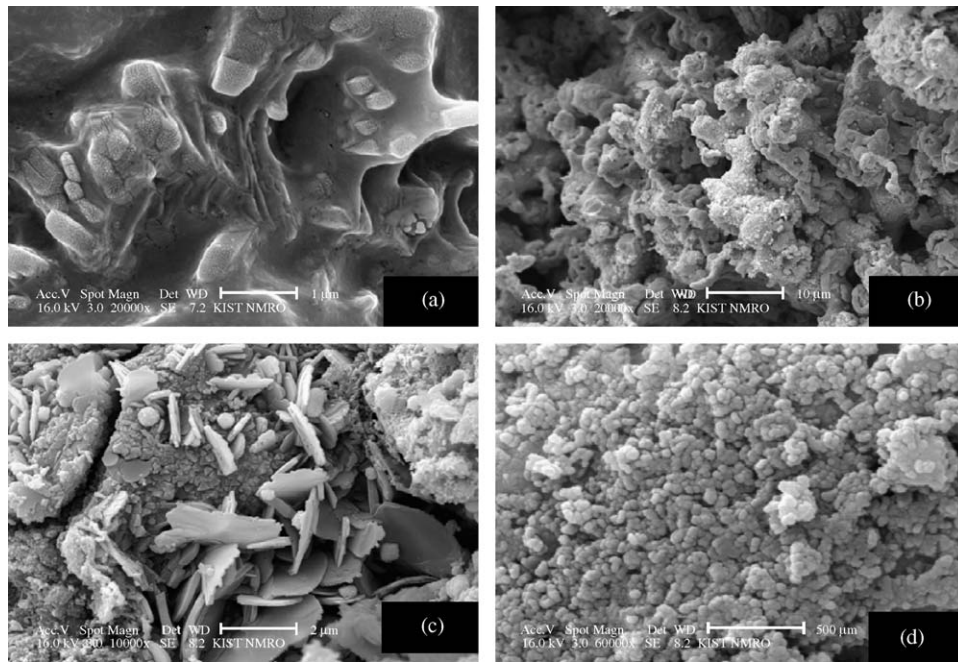


Fig. 5. Alumina particles: (a) before extraction of electrolyte, 20,000 \times , (b) after extraction of electrolyte, 2000 \times , (c) γ -LiAlO₂ on nickel surface, 10,000 \times , (d) α -LiAlO₂ on nickel surface, 50,000 \times .

Table 1
Physical properties of the components used in cell tests

Type of cell	Anode		Cathode		Additional electrolyte (mg cm ⁻²)
	Material	Porosity (%)	Material	Porosity (%)	
Standard cell	Ni-10 wt.% Cr	61	Lithiated NiO	67	–
Flooded cell	Ni-10 wt.% Cr	56	Lithiated NiO	68	50
Coated cell	Ni-10 wt.% Cr modified with bohemite sol	57	Lithiated NiO	68	50

It is useful tool to determine whether the cell is controlled by cathodic polarization, especially by mass-transfer reaction at the cathode. When the oxidant is switched from oxygen to air, concentration polarization is generated and the oxygen gain is increased because of the low oxygen partial pressure

[13]. The oxygen gains of both standard and modified cells are in the general range of 80 mV at 150 mA cm⁻², as shown in Fig. 8. For the standard cell with an excessive electrolyte, however, the oxygen gain is 175 mV. This difference is thought

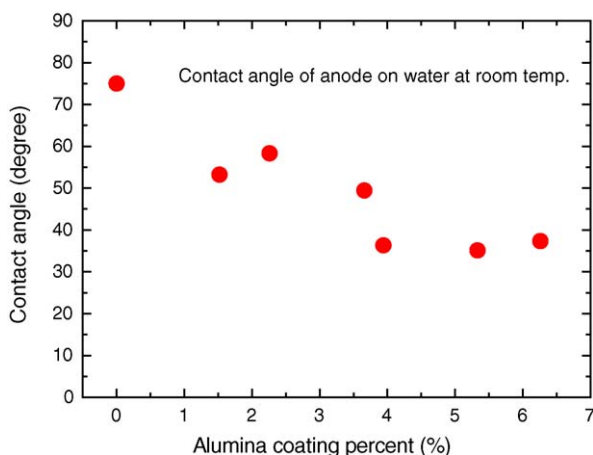


Fig. 6. Change of contact angles as function of coating amount.

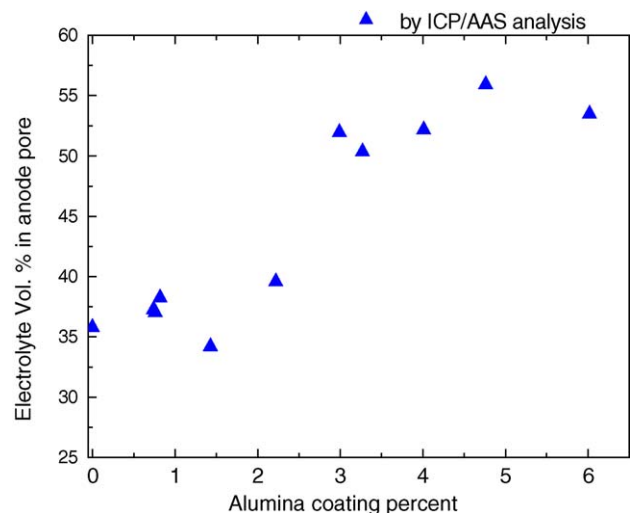


Fig. 7. Electrolyte filling content in anode (determined by ICP/AAS analysis).

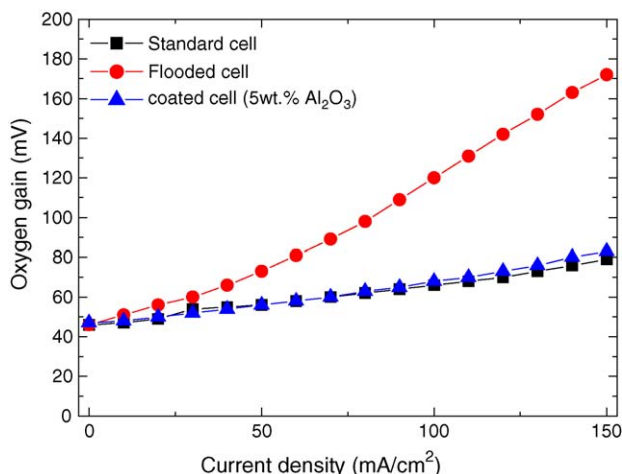


Fig. 8. Oxygen gains of various cells with different electrolyte loadings.

to be caused by an increase in concentration polarization due to cathode flooding by the excess electrolyte. On the other hand, even though there is sufficient electrolyte for flooding, the cell with the anode modified by the sol-gel coating shows a similar of oxygen gain to the standard cell (Fig. 8).

3.2.2. Performance

Three types of cell with different amounts of electrolyte loading were operated under the same condition. Both the standard cell and coated cell show a stable performance of around 0.8 V at 150 mV cm^{-2} . On the other hand, the performance of flooded cell is below 0.7 V at 150 mV cm^{-2} and rapidly decreases with operating time. At the start of cell operation, the low performance is attributed to cathode flooding, whereas at the end of cell operation the rapid decrease in cell performance is due to an outbreak of matrix cracking, which can be understood by an increase in the concentration of nitrogen at the anode outlet (Fig. 9(b)). With the present cell assembly, the additional electrolytes are added between the matrix green-sheets. If the additional electrolytes are not easily distributed to the electrodes, the surplus electrolyte in the matrix can destabilize the matrix structure. The coated cell in Fig. 9(c) exhibits similar I - V characteristics to the standard cell. This means that the anode modification exerts an effect on the distribution of additional electrolyte to the anode. As shown by the Nyquist plots in Fig. 10, both the internal resistance (IR) and the first arc of the impedance spectra show similar behaviour regardless of the amount of electrolyte in the cell. The last arc of the flooded cell, however, is larger than that of the other cells. It is not clear how many arcs are included in the impedance spectra neither is the electrochemical nature of these arcs fully understood. Since the last arc is more easily affected by gas phase diffusion, however, it is supposed that the last arc is related to the mass-transfer reaction. Therefore, the flooded cell, which suffers from the localization of excess electrolyte in the cathode, exhibits a larger last arc than either the standard cell or the coated cell.

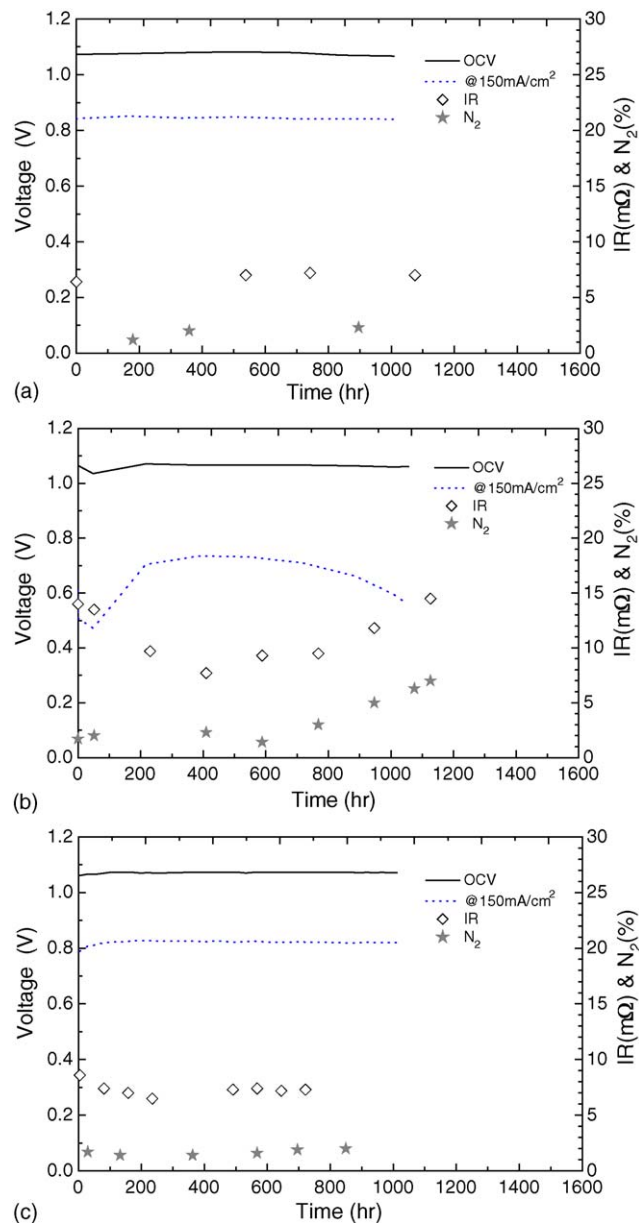


Fig. 9. I - V characteristics of various cells with different electrolyte loadings: (a) standard cell; (b) flooded cell; additional electrolyte of 50 mg cm^{-2} ; (c) coated cell, additional electrolyte of 50 mg cm^{-2} .

3.3. Post-analysis after cell operation

After cell operation, the electrolyte filling content of each component were investigated by the electrolyte extraction method. Contents are 27.5 mg cm^{-2} in the cathode and 12.5 mg cm^{-2} in the anode for the standard cell. In the flooded cell with a normal anode with excess electrolyte, however, the filling contents are 55.2 mg cm^{-2} in the cathode and 14.2 mg cm^{-2} in the anode, respectively. The surplus electrolyte in the cathode pores results in a decrease in cell performance (Fig. 9(b)) and an increase in the impedance spectra (Fig. 10). For the coated cell, even though it has the same amount of electrolyte as the flooded cell, the electrolyte filling content

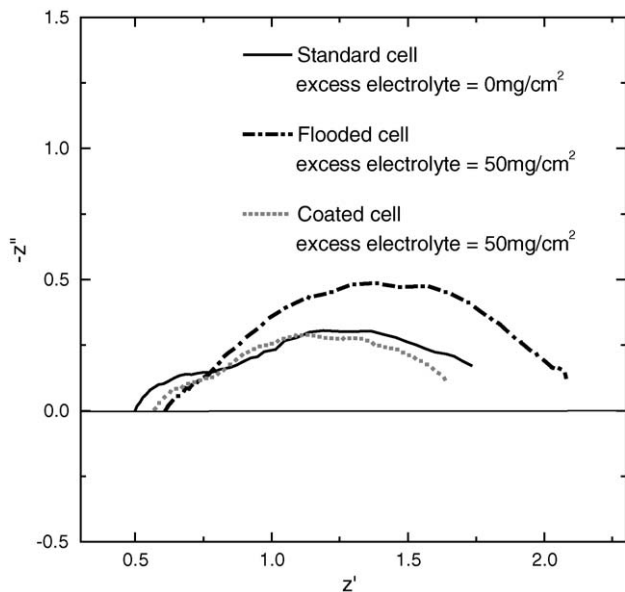


Fig. 10. Nyquist plots of various cells with different electrolyte loadings.

in the cathode (35.2 mg cm^{-2}) is similar to that in the standard cell (27.5 mg cm^{-2} , see Fig. 11). On the other hand, the anode is filled with 30.2 mg cm^{-2} , which is a large amount of electrolyte compared with that in the anode of the standard cell (12.5 mg cm^{-2}). This is attributed to an enhancement in the wettability by the surface modification of the anode, which can prevent the excess electrolyte from flooding into the cathode. For the coated cell, the surplus of electrolyte in the anode does not affect the cell performance, see Fig. 9(c), because of the fast electrochemical and mass-transfer reactions at the anode.

In order to examine the microstructures of the anodes after cell operations, the pore-size distribution after electrolyte extraction was analyzed. As shown in Fig. 12, the normal anodes in both the standard cell and the flooded cell have similar pore-size distributions. In the case of the modified anode, however, a microporous region (I) (less than the pore-size of the

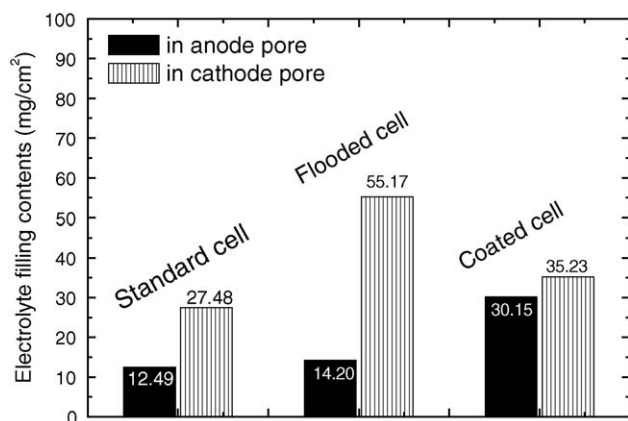


Fig. 11. Electrolyte filling content in anode and cathode pores of various cells with different electrolyte loadings.

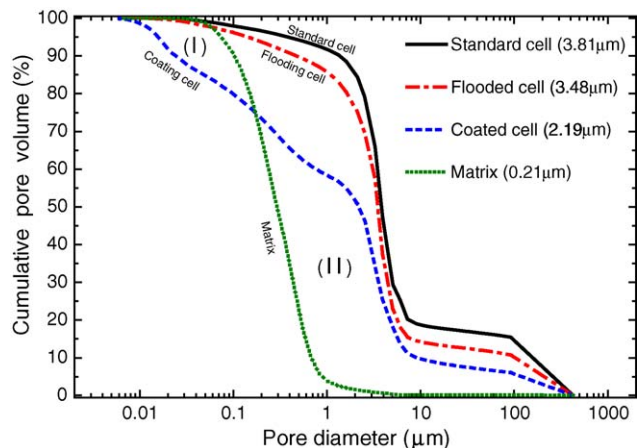


Fig. 12. Pore-size distribution of anode and matrix of various cells after cell operation.

matrix, $0.2 \mu\text{m}$) is produced during the cell operation. From the results, it is concluded that the prevention of cathode flooding from excessive electrolyte results from the production of micropores as well as an increase in the wettability on the anode.

4. Conclusions

For an electrolyte reservoir, the surface of an anode is modified with bohemite sol by using a dip-coating method. The coated film changes into lithium aluminate particles and produces micropores in the anode during cell operation. Consequently, the surface modification makes it possible to increase the electrolyte filling contents from 25–30 vol.% (12.5 mg cm^{-2}) to 50–60 vol.% (30.2 mg cm^{-2}) in the anode pores without any significant degradation in cell performance. In addition, the modification by the sol-gel coating technique induces an anti-sintering ability due to the lithium aluminate particles between the nickel particles. The results suggest that the surface modification can increase the structural stability of the anode, as well as the operation time, due to the additional electrolyte in the anode.

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