ELSEVIER

Addition of potassium tungstate to the electrolyte of a molten carbonate fuel cell

Seiji Terada [a,*], Kenjin Higaki [a], Ikuo Nagashima [a], Yasuhiko Ito [b]

[a] *Akashi Technical Institute, Kawasaki Heavy Industries, 1-1 Kawasaki-cho, Akashi, Hyogo 673-8666, Japan*
[b] *Graduate School of Energy Science, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan*

Abstract

Materials development for cell components is of great importance in prolonging the life of molten carbonate fuel cells because these systems operate at high temperature in corrosive environments. The effects of the addition of K_2WO_4 to the electrolyte are evaluated by out-of-cell tests and single-cell tests. The former tests show that K_2WO_4 addition effectively retards sintering of the anode, corrosion of the stainless-steel separator and phase transformation of the matrix substrate. Deposition of tungsten near the anode occurs in a cell test of 10,000 h. This suggests that tungsten suppresses the sintering of the anode. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Molten carbonate fuel cells; Electrolyte matrix; Anode sintering; Corrosion; Phase transformation

1. Introduction

Fuel-cell power generation systems are expected to be commercialized early in the 21st century because of their high efficiency and low emissions. The molten carbonate fuel cell (MCFC), in particular, has the potential for much higher efficiency and can use not only natural gas but also coal gas as a fuel. Because of the high operation temperature (923 K) and the presence of corrosive molten alkaline carbonate, however, degradation of the components can easily occur.

Greater cell life is one of the most important targets for MCFC to be brought into actual application. In this respect, investigators have proposed the addition of a tungsten salt such as K_2WO_4 to the electrolyte. This is supposed to retard sintering of the anode by forming precipitates through the reduction of tungstate with dissolved hydrogen near the anode surface [1]. In the research reported here, such an effect upon sintering of the anode has been examined by out-of-cell tests and the validity of the above speculation for the mechanism has been confirmed. Other effects of tungstate salt addition to the electrolyte on the corrosion of the separator, the solubility

of the cathode, and the stability of the matrix substrate [2] have also been investigated.

2. Experimental

2.1. Anode sintering

Sintering studies were conducted at 923 K using single cells, each with an active area of about 5 cm². A porous nickel plate with a pore volume of 0.19 cm³ g⁻¹ was used as the anode. A single cell was fabricated with two Ni porous gas-diffusion electrodes (30 mm diameter) and an electrolyte plate (50 mm diameter). The composition of the electrolyte was 62 mol% Li_2CO_3, 38 mol% K_2CO_3. A gas mixture of 72% H_2, 18% CO_2 and 10% H_2O was used to simulate the operating environment of a typical fuel cell anode. Pure CO_2 gas was used as the cathode gas to avoid oxidizing the anode, even if the cathode gas leaked to the anodic side. Anode samples were examined after sintering for 200, 500 and 1000 h. The pore volume of the sample was calculated from the value of bulk density measured after the carbonate salt contained in the samples was washed out with 10 vol.% acetic acid aqueous solution. The scheme used to study anode sintering is shown in Fig. 1.

* Corresponding author. Tel.: + 81-78-921-1636; fax: + 81-78-921-1689; E-mail: terada@ati.khi.co.jp
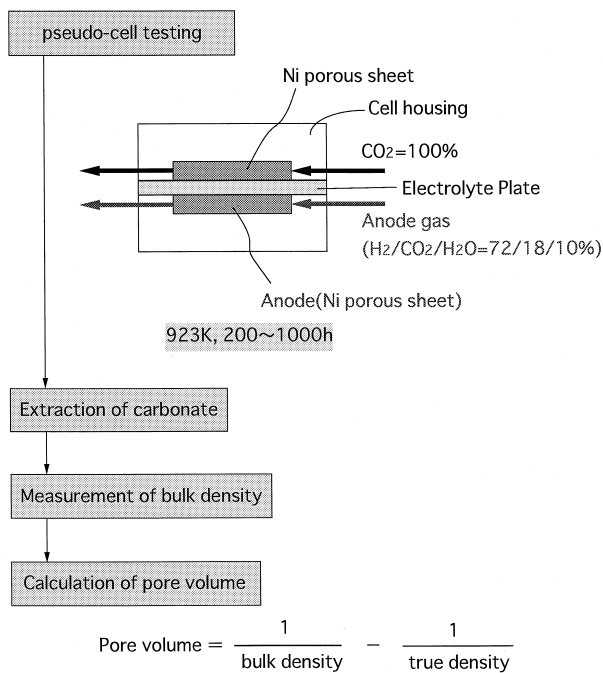
Fig. 1. Scheme of anode sintering test.

Penetration depth was measured by the difference between the value of upper site and the maximum value (at meniscus site) of test piece

Fig. 2. Scheme of corrosion test with partial immersion.

2.2. Corrosion of separator

Stainless-steel 316L specimens ($10 \times 30 \times 3$ mm) were used and immersed partially at 923 K for 150 h to examine the effect of the addition of K_2WO_4 to the electrolyte on corrosion of the separator. The carbonate mixture was 62 mol% Li_2CO_3, 38 mol% K_2CO_3 with the addition of 0, 1.4 and 5.6 wt.% K_2WO_4. The atmospheric gas used in the experiments was 30% CO_2–15% O_2–55% N_2 or 10% CO_2–15% O_2–75% N_2. After immersion for 150 h, the oxide scale on the test specimens was removed by putting the specimens into a 18% $NaOH + 3\%$ $KMnO_4$ boiled solution, 10% ammonium citrate solution, and then washed in acetone with ultrasonic cleaning. After the oxide scale was removed, the penetration depth of the specimens was measured with a thickness meter. The scheme of these tests is shown in Fig. 2.

2.3. Cathode dissolution

Experimental solubilities were determined as follows. One gram of a slightly sintered NiO pellet (1 to 2 mm in diameter) and 150 g of the carbonate were contained in a pure alumina crucible, over which was passed the desired mixture of CO_2, O_2 and N_2.

The carbonate mixtures used in this experiment were 62 mol% Li_2CO_3, 38 mol% K_2CO_3 and 52 mol% Li_2CO_3, 48 mol% Na_2CO_3. The addition of K_2WO_4 was 7.0 wt.% in the molten carbonate. Samples of the melt were periodically removed from the crucibles with an alumina pipette. The samples were diluted in acetic acid and, in order to avoid the influence of the tungsten peak, the dissolved
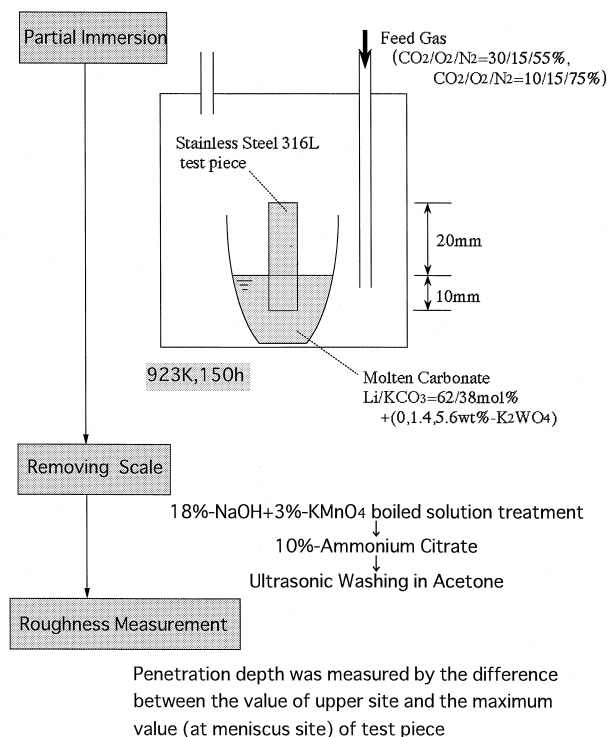
nickel was extracted into chloroform by putting the sample into a mixture of dimethyl glyoxime and chloroform. The nickel content was determined by ICP analysis. The scheme of the cathode dissolution test is shown in Fig. 3.
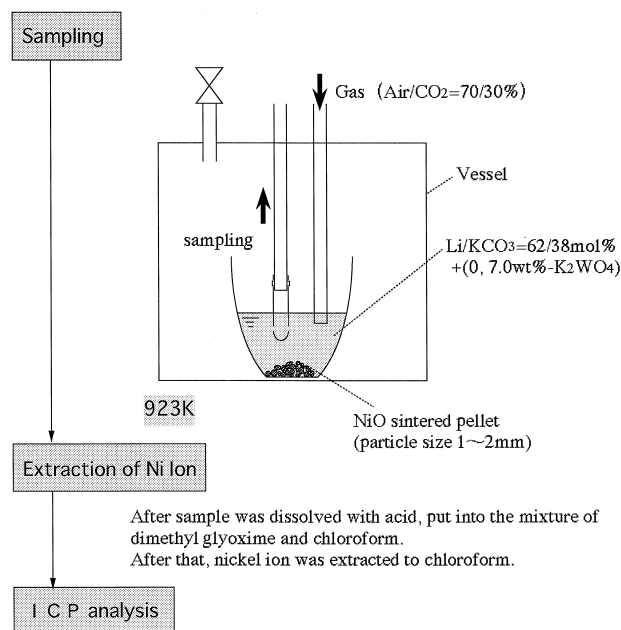

After sample was dissolved with acid, put into the mixture of dimethyl glyoxime and chloroform.
After that, nickel ion was extracted to chloroform.

Fig. 3. Scheme of NiO solubility measurement.
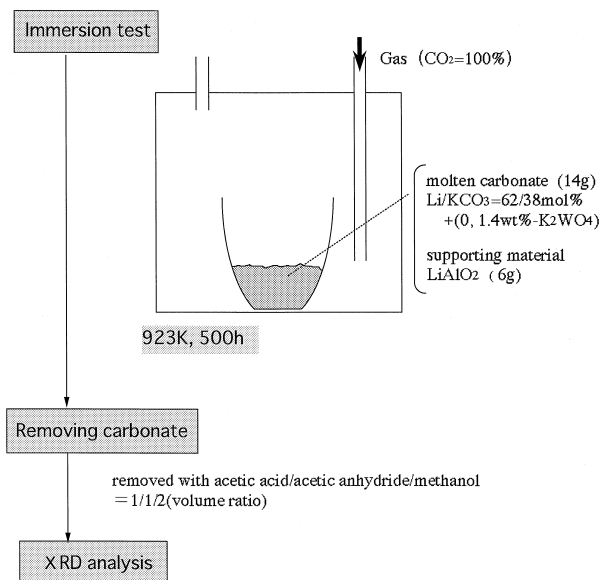
Fig. 4. Immersion test on the stability of $LiAlO_2$.

Fig. 5. Influence of tungstate addition on anode pore volume.

2.4. Phase transformation of $LiAlO_2$

Immersion tests were conducted to investigate the effect of K_2WO_4 addition to the electrolyte on the stability of the electrolyte supporting material, $LiAlO_2$. The carbonate mixture used in this experiment was 62 mol% Li_2CO_3, 38 mol% K_2CO_3. The carbonate (14.000 g), the lithium aluminate (6.000 g) and K_2WO_4 (0.000 or 0.196 g) were mixed and contained in a crucible made from 99.5% pure alumina. The immersion tests were conducted for 500 h at 923 K in pure CO_2. The lithium aluminate particles were washed with a 1:1:2 mixture of acetic acid, acetic anhydride and methanol, and then dried. The phase was identified by X-ray diffraction (XRD) analysis. The scheme of these immersion tests is shown in Fig. 4.

2.5. Endurance test

Endurance tests were conducted in a 100-cm^2 single cell for more than 10,000 h in order to verify the effect of potassium tungstate added to the matrix. An Ni or Ni–Al anode and an NiO cathode, both 100 cm^2, were used in the single cells. The composition of the carbonate was 62 mol% Li_2CO_3, 38 mol% K_2CO_3 with the addition of 1.4 wt.% K_2WO_4. The wet seal part of the cell housing was coated with aluminum to avoid deterioration due to electrolyte loss. Cells were normally operated at a continuous current of 150 mA/cm^{-2}.

3. Results and discussion

3.1. Anode sintering

In an operating fuel cell, substantial change in the pore volume of the anode is unacceptable. Changes of pore
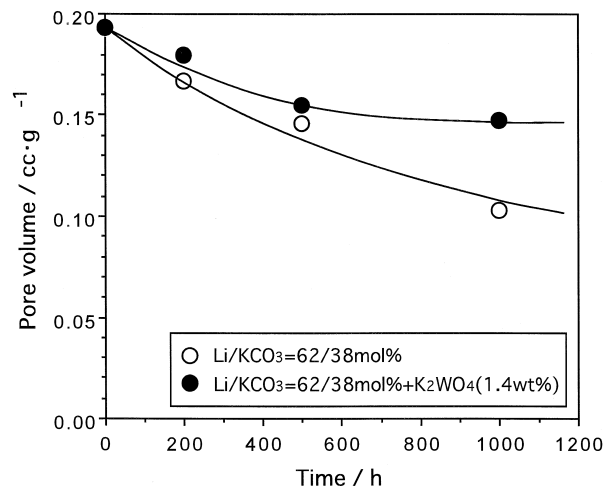
volume with time are shown in Fig. 5 with or without K_2WO_4 additions. Porous nickel anodes without K_2WO_4 additions exhibit a substantial loss of pore volume, although appreciable sintering did occur. By contrast, the loss of pore volume in porous nickel anodes with K_2WO_4 additions is substantially decreased; there is an initial drop in pore volume over 400 h but little change thereafter ($\sim 80\%$ of initial value after 1000 h). This effect is due to reduction of tungstate ion to produce tungsten metal on the porous nickel electrode under a hydrogen atmosphere [1].

3.2. Corrosion of separator

The results of corrosion studies using stainless-steel 316L test pieces under cathode conditions are shown in Fig. 6. Potassium tungstate addition has some effect on the corrosiveness of the melt and minimum corrosion was
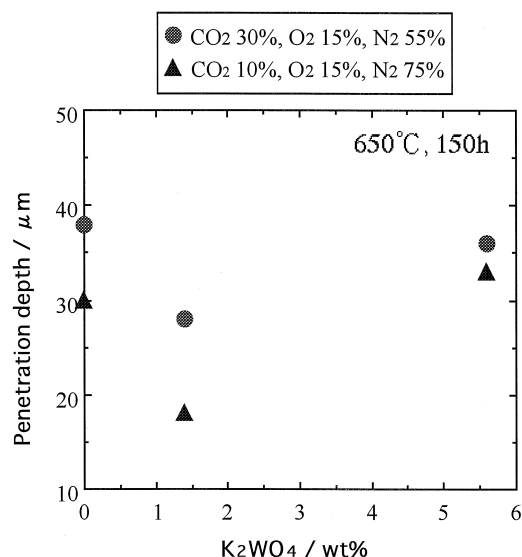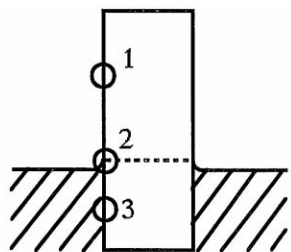

Fig. 6. Influence of tungstate addition on SUS316L corrosion.

650℃

10 % CO$_2$ - 15 % O$_2$ - 75 % N$_2$

62 mol%Li$_2$CO$_3$ - 38 mol% K$_2$CO$_3$

	No addition	K$_2$WO$_4$ addition ; 1.4 wt%
1		
2		
3		

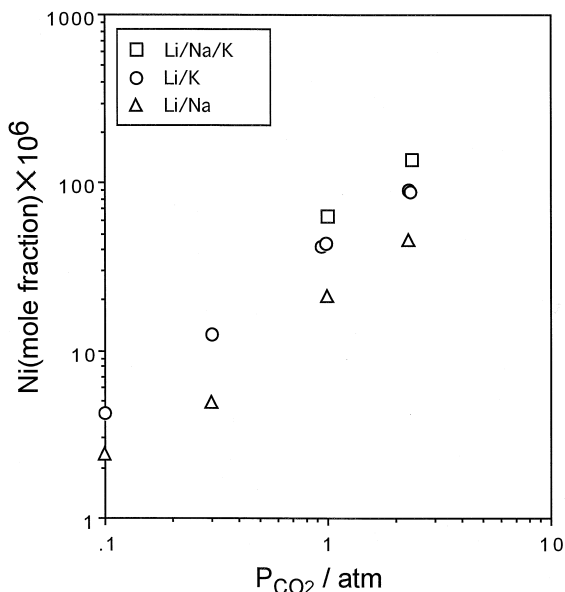Fig. 7. Influence of tungstate addition on corroson of stainless-steel 316L.

Fig. 8. Influence of molten carbonate on CO_2 partial pressure and NiO solubility.

attained at 1.4 wt.% addition of potassium tungstate. Photographs of the cross-sections of test pieces after immersion for 150 h at 923 K in a 10% CO_2–15% O_2–75% N_2 atmosphere are shown in Fig. 7. In the absence of potassium tungstate, the oxide scale at the central part of the test piece fell off and can be considered to penetrate the substrate by corrosion. When 1.4 wt.% potassium tungstate was added to the electrolyte, a thick film was formed and was considered to decrease the rate of corrosion.

In general, oxy-anions including carbonate ion tend to dissociate oxide ion, O^{2-}, and to affect the basicity of the melts. Tungstate ion, WO_4^{2-}, is supposed to act similarly
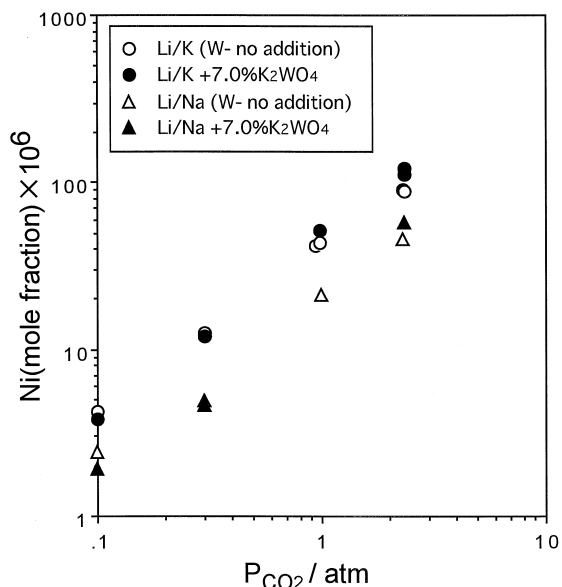
and possibly to have some influence on the corrosion of the separator material by the melt.

3.3. Cathode dissolution

The solubility of NiO vs. partial pressure of CO_2 in an Li/K carbonate system and an Li/Na carbonate system without K_2WO_4 addition is shown in Fig. 8. The solubility of transition metal oxides is thought to be a function of the acid/base chemistry of the melt that is controlled by the CO_2 partial pressure of the oxidant gas and the change in the carbonate melt composition (for example, increases in the lithium content in Li:K carbonate). For the acidic dissolution of NiO in molten carbonates, the solubility of the oxide decreases with increasing oxide activity of the melt (increasing basicity). This behaviour is demonstrated clearly in Fig. 8.

The solubility of NiO vs. partial pressure of CO_2 in an Li:K carbonate system and an Li:Na carbonate system both with and without K_2WO_4 addition is shown in Fig. 9. The solubility of an NiO cathode is slightly lowered by the presence of the tungstate salt in a low CO_2 environment, but is not affected under normal operational conditions.

3.4. Phase transformation of $LiAlO_2$

The phase transformation and growth of $LiAlO_2$ particles, observed during prolonged cell operation, is a serious problem to overcome in order to attain a life of more than 40,000 h for an MCFC because it causes pore coarsening
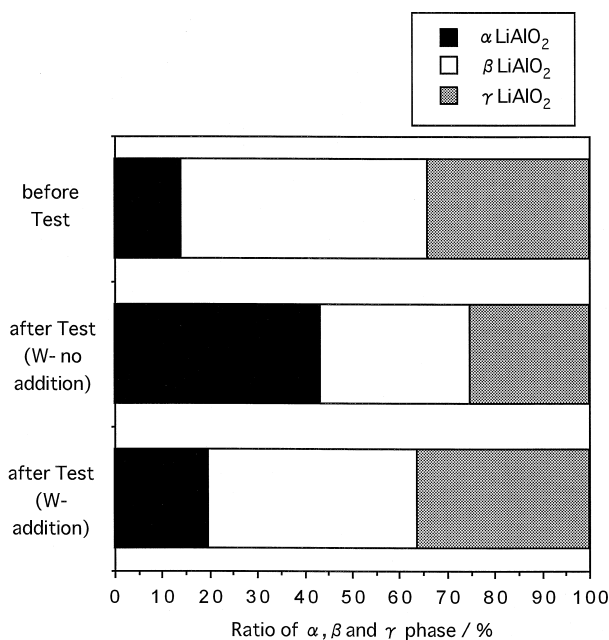

Fig. 9. Influence of tungstate addition on NiO solubility.

Fig. 10. Influence of tungstate addition on phase transformation of $LiAlO_2$. Test conditions — matrix: HSA-19; electrolyte: Li/KCO$_3$-(62/38), Li/KCO$_3$(62/38)+1.4 wt.% K_2WO_4; temperature: 650°C; gas: CO_2; time: 500 h.
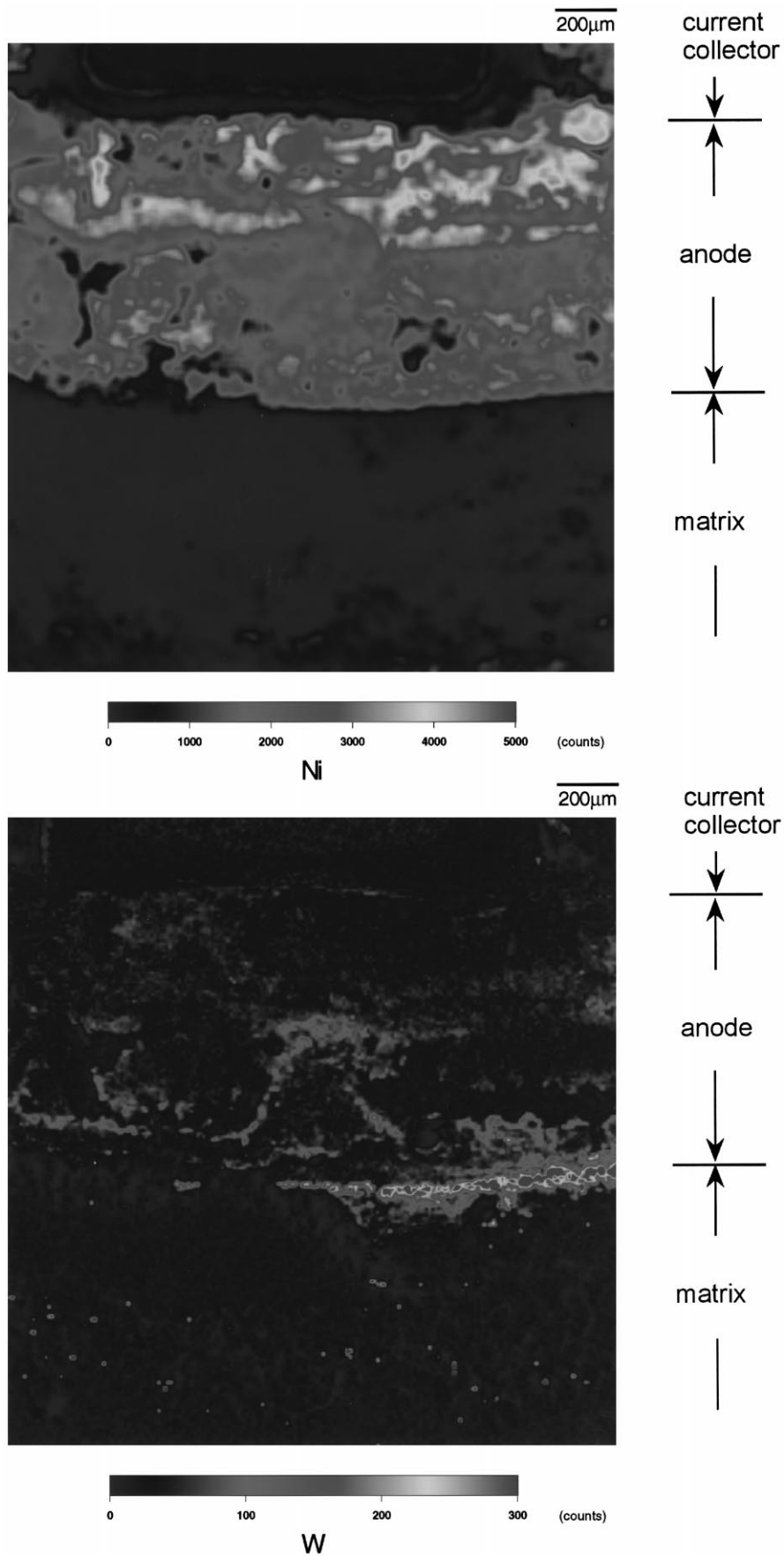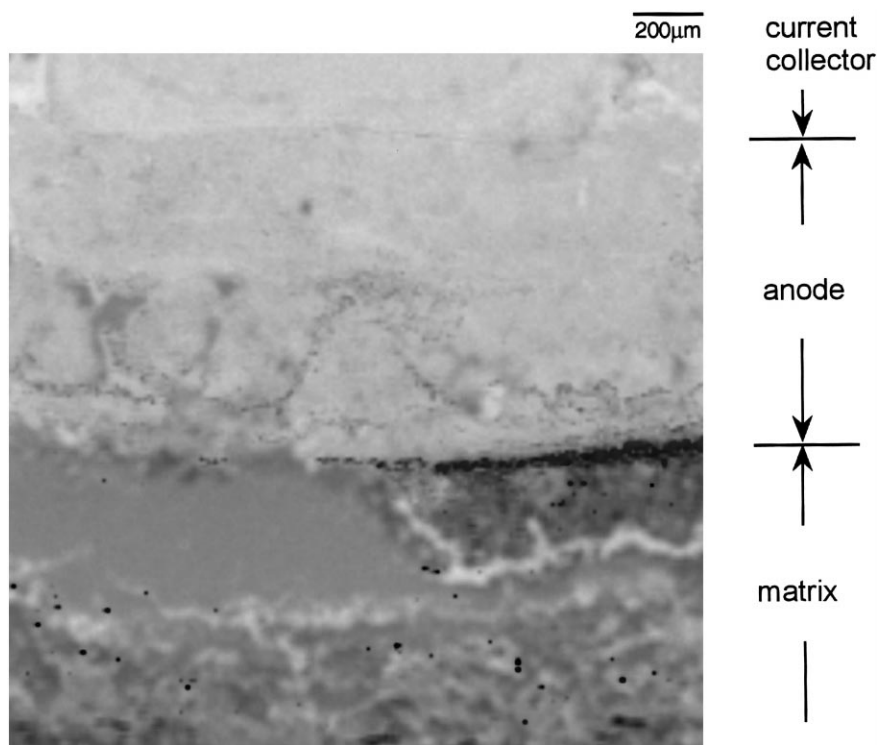
Fig. 11. EPMA analysis after 10,000 h operation.

Fig. 11 (continued).

of the porous matrix substrate and less capillary force to retain the electrolyte in its pores. Out-of-cell tests, in which $LiAlO_2$ powders are impregnated in melts, have been conducted and the effect of various parameters on phase transformation and particle growth of $LiAlO_2$, including tungstate salt addition to melt, have been investigated. An example of the phase transformation of $LiAlO_2$ at CO_2 ambient is presented in Fig. 10. There is an increase in the α phase and decreases in the β and γ phases in the absence of tungstate. The corresponding changes in phase transformation are small in the presence of tungstate. In particular, there is a slight increase in the γ phase. The mechanism of phase transformation and particle growth of $LiAlO_2$ in molten carbonates are reported in the previous paper [2].

3.5. Endurance test

EPMA analysis was used to determine the distribution of tungsten concentration across the anode and the electrolyte matrix after 10,000 h cell operation when using a pure Ni anode (Fig. 11). The concentration of tungsten at the anode is higher than that at the matrix. This means that tungstate ion, WO_4^{2-}, converts into other insoluble compounds at the anode as a sink and the diffusion of WO_4^{2-} ions from the matrix to the anode occurs. Such compounds of tungsten are supposed to be formed through reduction

of WO_4^{2-} ions by dissolved hydrogen in the electrolyte. These compounds precipitate around the anode particles and retard the sintering of Ni anode.

The performance of a 100-cm^2 class cell using an Ni–Al porous anode with 1.4 wt.% K_2WO_4 addition in the electrolyte is given in Fig. 12. The cell was operated for more than 10,000 h without electrolyte replenishment.
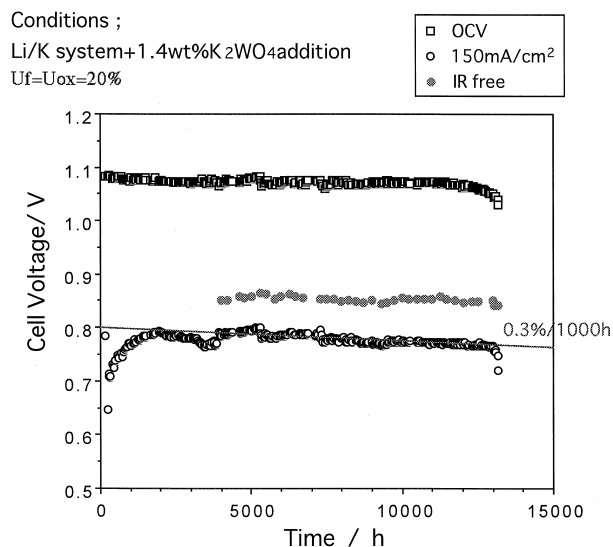

Fig. 12. Cell performance of a single-cell test.

After 13,000 h, the cell performance drastically dropped because a short-circuit occurred abruptly by NiO cathode dissolution–precipitation. The degradation rate of voltage up to 13,000 h was less than 0.3%/1000 h. Thus, it is confirmed that the addition of potassium tungstate to the electrolyte of an MCFC is effective for a long life.

4. Conclusions

The effects of tungstate salt addition to the electrolyte of MCFCs on cell characteristics have been clarified. The results are summarized as follows.

(i) Sintering of the porous nickel electrode can be retarded by addition of tungstate salt. This effect is due to the reduction of tungstate ions to produce tungsten metal on the porous nickel electrode under a hydrogen atmosphere.

(ii) Corrosion tests using stainless-steel 316L test pieces under cathode conditions show that addition of potassium tungstate exerts some effect on the corrosiveness of the melt and minimum corrosion is attained at an addition of 1.4 wt.% potassium tungstate.

(iii) The solubility of NiO cathode is slightly lowered by tungstate salt in a low CO_2 environment, but is not affected under normal operational conditions.

(iv) The addition of K_2WO_4 to the electrolyte is effective in suppressing the phase transformation of $LiAlO_2$, including the α, β and γ phases.

(v) A 100-cm^2 single cell using an Ni–Al porous anode with 1.4 wt.% K_2WO_4 added to the electrolyte has been operated for more than 10,000 h with a degradation rate of less than 0.3%/1000 h.

Acknowledgements

References

[1] G. Xie, K. Ema, Y. Ito, J. Power Sources 35 (1991) 123.
[2] S. Terada, I. Nagashima, K. Higaki, Y. Ito, J. Power Sources 75 (1998) 223.