

A Simple Surface Modification of NiO Cathode with TiO₂ Nano-Particles for Molten Carbonate Fuel Cells (MCFCs)

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Molten carbonate fuel cells (MCFCs) are efficient energy conversion devices to convert chemical energy into electrical energy through the electrochemical reaction.^{1,2} Because of a lot of advantages of MCFC operated at high temperature, many researchers have been trying to apply it to large-scaled power generations, marine boats, and so on.^{1,2} Among various cathode materials, nickel oxide, NiO, is the most widely used cathode for MCFCs due to its stability and high electrical conductivity, but the degradation of cathode material, so-called NiO dissolution, prevents a long-term operation of MCFC.^{1,3} In order to overcome the drawback, numerous studies have been performed. One of the most useful ways to enhance the surface property and maintain the bulk property of the host materials is the surface modification.⁴ The most common modification method is coating and these coating procedures which need some complicated steps with the use of organic materials,^{3,5} but it restricts the large-scale fabrication.⁴ In this study, to improve the electrochemical performance, we have prepared an alternative MCFC cathode material, TiO₂-modified NiO, by simple method without resorting to any complex coating process. Results obtained in this study can provide an effective way to mass-produce the cathode materials applied to MCFC.

The TiO₂-modified Ni powder was prepared by a simple method, ball-milling and subsequent annealing. The ball-milling was carried out for various periods (5, 10, 24, and 42 h) and it is found that TiO₂ nano-particles do not considerably adhere to the Ni powder for short-time (less than 10 h). However, after 24 h of ball-milling, the surface of the Ni powder is homogeneously covered by TiO₂ nano-particles. The ball-milling of Ni powders with titania nano-particles do not cause any significant morphological change of Ni particle and results in well-distribution of titania nano-particles on the surface of the Ni powder. After ball-milling, TiO₂ nano-particles are physically bound onto Ni and they are likely to be detached during slurry preparation and/or tape casting processes. To avoid unwanted detachment of TiO₂, the ball-milled powder was annealed. To determine the annealing temperature, dispersion tests⁴ with the powder annealed at various temperatures (200-650 °C) were performed. From the results of dispersion tests, the powder

annealed below 500 °C shows the TiO₂ nano-particles floating in the solvent. On the other hand, the samples annealed above 500 °C do not disperse in the solvent but sink instantly. Therefore, the annealing above 500 °C provides the formation of chemical binding between TiO₂ and Ni. Figure 1 shows the morphologies of the powder samples, annealed at 650 °C for 10 h, measured by scanning electron microscopy (SEM). The tiny particles, which bound onto Ni surface after ball-milling, disappear and the surface of powder samples is much smoother than that of pristine and ball-milled powder samples. The particle size of the TiO₂-modified powder is almost same as that of the pristine NiO powder. The existence of Ti is identified through energy dispersive spectroscopy (EDS) and these data demonstrate the homogeneous distribution of Ti without severe agglomeration after annealing.

The structural change in the modified powders after surface modification was investigated by X-ray diffraction (XRD). Figure 2 shows XRD data of the samples annealed at 650 °C for 10 h as a function of the composition of TiO₂. The XRD

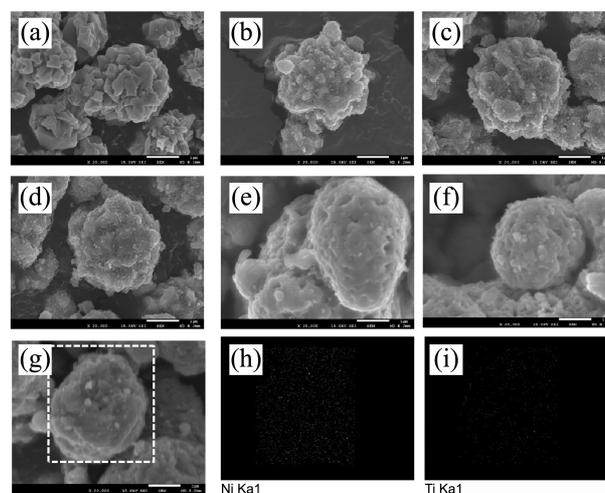


Figure 1. SEM and EDS images of TiO₂-modified powder samples. (a) pristine Ni powder, (b)-(d) ball-milled powder samples (1.00 mol %, 1.75 mol %, and 2.50 mol % TiO₂-modified), (e)-(g) annealed powder samples (1.00 mol %, 1.75 mol %, and 2.50 mol % TiO₂-modified), (h)-(i) EDS mapping images of Ni and Ti for (g).

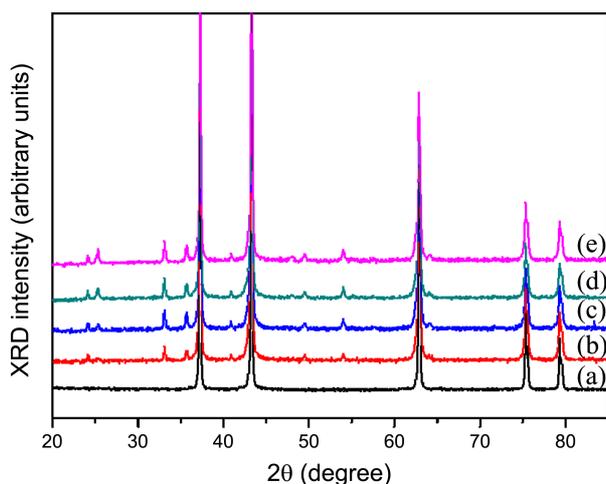


Figure 2. XRD data of various TiO₂-modified NiO powders after ball-milling and subsequent annealing at 650 °C for 10 h: (a) pristine NiO, (b) 1.00 mol %, (c) 1.75 mol %, (d) 2.50 mol %, and (e) 2.75 mol % TiO₂-modified powders.

data for the pristine Ni powder annealed at 650 °C shows the intense peaks at 37.2, 43.3, 62.9, 75.4, and 79.4° assigned to the characteristic features of NiO (JCPDS #47-1049). The TiO₂-modified NiO powders show small TiO₂ diffraction features at 25.3, 37.8, 48.1, and 53.9° (JCPDS #21-1272) and some additional features are observed at 33.09, 35.65, and 54.01° (JCPDS #33-0960). These diffraction features are assigned to NiTiO₃ which is formed by the reaction of TiO₂ and Ni at 650 °C. At very low concentration of TiO₂, the most abundant phase other than NiO is NiTiO₃, but the intensity of NiTiO₃ features is saturated and the intensity of TiO₂ features increases as the content of TiO₂ increases. Moreover, with increasing the annealing temperature, the XRD features of TiO₂ disappear and the NiTiO₃ features become more intense (not shown for brevity). It indicates that the diffusion rates of Ti and/or reaction kinetics are not quite fast at 650 °C and the excess amount of TiO₂ is left over. It is well-known that NiTiO₃ is formed from NiO and TiO₂ at high temperature and the mixture of NiO and TiO₂ at high temperature forms NiTiO₃ and (Ni, Ti)O solid solutions.⁶ This passive surface layers play an important role in suppressing NiO dissolution which is the most serious problem in MCFC operation.

The Ni solubilities⁴ of the pristine and modified NiO cathodes in molten carbonates media were performed and the results are shown in Table 1. Whereas the Ni concentration for the pristine NiO cathode in molten carbonates is 33.5 ppm on the average, the Ni concentrations for the TiO₂-modified NiO cathodes were less than ~20 ppm and that for 2.5 mol % TiO₂-modified sample was 16.0 ppm. The concentration of Ni in the molten carbonate for the modified cathode is significantly reduced in comparison with the pristine cathode. Several previous studies have theoretically⁷ and/or experimentally⁸ shown that titanium species in a molten carbonates media is the stable species. Chauvaut *et al.*⁷ reported that titanium species in a molten carbonate

Table 1. Porosity for various cathodes and ICP-MS data of the concentration of Ni for cathodes kept in the molten carbonates at 650 °C for 300 h

Cathode	Porosity (%)	Concentration of Ni (ppm)
Pristine Ni (750 °C for 30 min)	79.40	33.53
1.00 mol % TiO ₂ (750 °C for 5 h)	77.12	20.11
1.75 mol % TiO ₂ (750 °C for 5 h)	75.10	17.96
2.50 mol % TiO ₂ (750 °C for 5 h)	76.90	16.03
2.75 mol % TiO ₂ (850 °C for 5 h)	65.30	12.96

medium form lithium titanate which is the stable species all over the acidity range. Zeng and Wu⁸ also reported that Ni-Ti alloy (with low concentration of Ti) in molten carbonates reduces its corrosion rate significantly in comparison with pristine Ni by forming an external scale containing NiO and TiO₂. Hence, the TiO₂-modified NiO forms the stable protective layers on the surface and consequently reduces the Ni dissolution in molten carbonates media. Moreover, the remarkable decrease in solubility is also attributed to the formation of stable Li₂TiO₃ and/or LiTi_{1-x}NiO₃ phases⁹ which reduce the dissolution of Ni²⁺ ions into the electrolyte during MCFC operation. In this study, due to the low concentration of Ti and the overlap of XRD features of the lithiated phase with NiO, Li₂TiO₃ and LiTi_{1-x}NiO₃ phase could not be directly observed. However, Hong *et al.*⁹ previously confirmed that the TiO₂ reacts with Li in molten carbonate to form Li₂TiO₃ during immersion in molten carbonate from result of the Raman spectra of TiO₂-modified Ni powder obtained after immersion in molten carbonate.⁹ Figure 3 shows the XRD data after lithiation test at 650 °C for 300 h. The main peak of NiO of the TiO₂-modified Ni powder shifts to higher angles in comparison with that of pristine NiO powder. The peak shift¹⁰ is attributed that the introduction of more Li⁺ ions into the NiO lattice and the solid solutions. The peak shift in the XRD results is also observed after the cell operation for 300 h. Furthermore, the lithiation of cathode material during the cell operation enhances the electrical conductivity.

The electrochemical performance was investigated by the unit cell test.⁴ The performance of unit cells employing the pristine Ni and TiO₂-modified Ni cathodes are compared under cathode gas conditions of CO₂:O₂ (33:67%). Figure 4 shows open circuit voltages (OCVs) and closed-circuit voltages (CCVs) at 150 mA/cm² of current density at 650 °C as a function of operation time. The cell with the pristine NiO cathode shows that OCV and CCV are 1.12 and 0.87 V, respectively. On the other hand, the cell with TiO₂-modified cathode shows the higher CCV as an increase in the content of TiO₂. The maximum CCV (0.93 V at 150 mA/cm²) is obtained with a cell consisting of 2.50 mol % TiO₂-modified cathode. However, a cell with 2.75 mol % TiO₂-modified cathode sintered at high temperature shows poor performance and lowest CCVs due to its low porosity (65.30%) in comparison with other cathodes as shown in Table 1. The enhanced cell performance for the modified cathode in

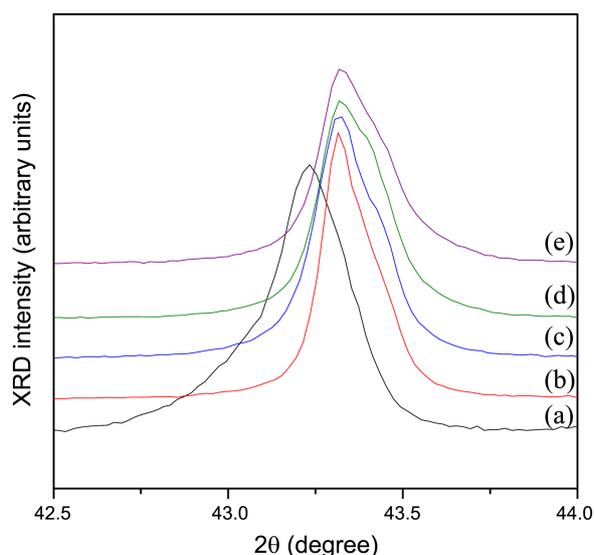


Figure 3. XRD data of the NiO powder after lithiation test at 650 °C for 300 h; (a) pristine NiO powder, (b) 1.00 mol % TiO₂, (c) 1.75 mol % TiO₂, (d) 2.50 mol % TiO₂, and (e) 2.75 mol % TiO₂-modified NiO powder.

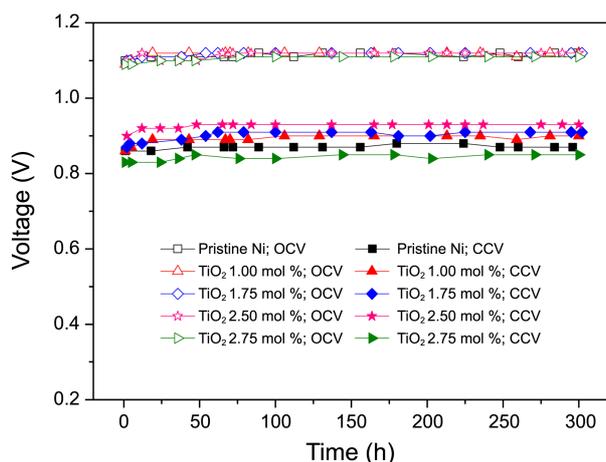


Figure 4. The results of unit cell performance test: open circuit voltages (OCVs) and closed circuit voltages (CCVs) for various cathodes at 150 mA/cm² of current density as a function of operation time.

comparison with pristine NiO cathode is attributed to the improved electrical conductivity by the formation of NiTiO₃ phase and the higher degree of lithiation as shown in Figure 3.

Figure 5 shows the cell potentials and power densities as a function of current density. At very low current density, the cell voltages are not significantly different among cells with pristine or modified cathodes. As an increase in the current density, the cell with modified cathode has higher CCV and power density. Singh *et al.*¹¹ reported that the activation energy of NiTiO₃ for electrical conduction at high temperature is significantly lower than that of NiO. Hence, the phase of NiTiO₃ formed by the reaction of NiO and TiO₂ provides higher electrical conductivity and it improves the cell performance. Furthermore, the lithiation of cathode material during the cell operation also enhances its electrical

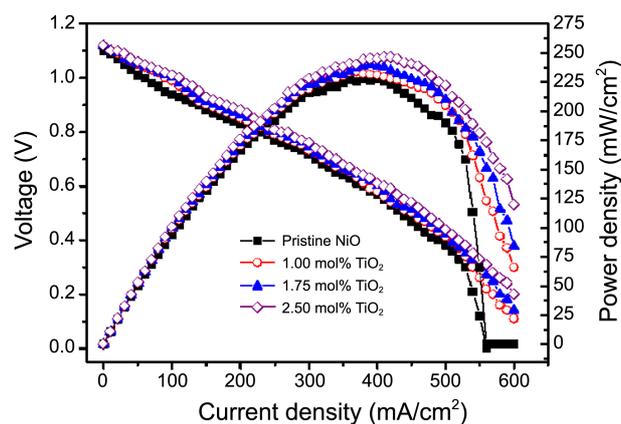


Figure 5. Voltage and power density data for MCFC with various TiO₂-modified NiO cathodes as a function of current density.

conductivity. After lithiation of cathode, XRD data of NiO shifts to a higher angle direction as shown in Figure 3. Therefore, the appropriate porosity, the enhanced electrical conductivity and the higher degree of lithiation for the modified cathode improves cell performance in comparison with pristine NiO cathode.

In conclusion, the TiO₂-modified Ni powders, prepared by the simple method (ball-milling and subsequent annealing) without resorting to any complex coating process, eventually form nickel titanate passive layer at high temperature. It has good corrosion resistance in molten carbonates media and higher electrical conductivity at high temperature. In addition, the modified cathode increases the degree of lithiation during the operation of MCFC. These positive effects provide a decrease in the internal resistance and improve the cell performance. Results obtained from this study can be applied to develop the surface modification of cathode materials and the performance of molten carbonate fuel cells.

Experimental

TiO₂-modified Ni Powder. TiO₂-modified Ni powder was prepared by ball-milling of TiO₂ powder (particle size ≤ 25 nm, Aldrich) and Ni powder (particle size = 2-3 mm, Inco nickel 255). The sample powders were prepared with various mole ratios of TiO₂ (1.00, 1.75, 2.50, and 2.75 mol %). The ball-milled powder samples were annealed at various temperatures (200-650 °C) for 10 h under ambient condition. In order to set the annealing temperature, the dispersion test⁴ was performed. About 0.020 g of Ni powder and TiO₂-modified Ni powder with oxidation for annealing or without, are immersed into 5 mL of solvent which is same composition of slurry (ethanol: toluene = 70:30 wt %). The mixture is ultra-sonicated for one minute. After the sonication, the status of powder in solvent is observed.⁴

TiO₂-modified Ni Cathode. The TiO₂-modified cathode was prepared by tape casting with TiO₂-modified Ni powder and slurry after ball-milling for 5 h. The slurry was composed binder (polyvinyl butyral, Monsanto), plasticizer (dibutyl

phthalate, Junsei), dispersant (Disper BYK-110), defoamer (Dappo D354) and solvent (ethanol:toluene = 70:30 wt %, Junsei).^{4,9,12,13} After ball-milling and degassing using a rotary evaporator with stirring for mixing of slurry with TiO₂-modified Ni powder, the green sheet with 0.7-0.8 mm thickness was obtained by tape casting using double doctor blade. The green sheet dried at room temperature for 24 h was sintered under the reducing atmosphere (Ar:H₂ = 70:30%).

Lithiation and Solubility Tests. The degree of lithiation of the cathode and the concentration of Ni in the electrolyte were investigated in the equivalent condition as MCFC operation.^{4,5,9,12-14} For lithiation test, 1.5 g of modified powder and 100 g of (Li/K)₂CO₃ (62/38 mol %) was transferred to alumina crucible, and heated to 650 °C under CO₂:O₂ (67:33%) atmosphere. After 300 h, the powder sample was collected and cleaned with 1.0 M acetic acid solution to get rid of carbonates on the surface, and then washed with distilled water and dried. The structure and the surface morphology of the samples were investigated by X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). For solubility test, the experimental procedure is identical to that of lithiation test except for the sample which is not powder but sintered electrode.^{4,5,9,12-14} Periodically ~0.30 g of molten carbonate was collected using alumina pipette to measure the concentration of Ni in the molten carbonate. The solidified carbonates were dissolved in 1.0 M HNO₃ solution. After the solvent was evaporated, it was diluted with 20 mL of distilled water. Concentration of Ni dissolved into the molten carbonates was measured with inductively coupled plasma atomic emission spectroscopy (ICP-AES, JY Ultima2C (Jobin Yvon, France) or inductively coupled plasma mass spectroscopy (ICP-MS, Elan DRC II / Perkin Elmer, USA).

Unit Cell Operation. The performance of unit cell was operated using 3 × 3 cm² cell at 650 °C for 300 h. The open circuit and the closed circuit voltages at current density of 150 mA/cm² were measured. Except the cathodes, other components of cell were commercial products.^{4,5,9,12-14} The

anode gas was H₂/CO₂ (67:33%) humidified at 50 °C, and the cathode gas was CO₂:O₂ (67:33%) or air:CO₂ (70:30%). To investigate the electrochemical properties of prepared cathode materials, electrochemical impedance spectroscopy (EIS) was employed in with an IM6 electrochemical analyzer (ZAHNER elektrik, Germany). The frequency range was 10 MHz to 100 kHz with a rate of 20 point per decade. The amplitude of sinusoidal voltage signal for the impedance analyzer was 5 mV.

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