

## Investigations of the Mechanism of Dissolution and Deformation for NiO Cathode Materials in MCFC

Li-Jiang Chen, Chang-Jian Lin, Xuan Cheng, Zu-De Feng

Dept. Chemistry, Dept. Materials Science, State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen, China 361005  
cjlin@xmu.edu.cn

From a long-term view molten carbonate fuel cell (MCFC) will be the only kind fuel cell applied to generating electricity of main force in the future owing to its high efficiency of generating electricity. However the molten alkaline metal carbonates used in MCFC result in a short cell lifetime because of severe dissolution and deformation of NiO cathode material. Thereinto the dissolution and deformation of NiO cathode material is a major problem in the MCFC development. In order to decrease the dissolution and deformation for the cathode material, it is very important to clarify the mechanism of cathode dissolution for prolonging the lifetime of cathode materials in MCFC.

An in-situ Raman spectroscopic technique was developed to study the dynamic behavior of cathode reaction involved in MCFC. And owing to its high sensitivity, in-situ measurement and control facility of testing conditions, it is very powerful to elucidate the dissolution and degradation mechanism of NiO material at molecular level. In MCFC  $\text{CO}_2$  tends to adsorb strongly on the surface of NiO, and it belongs to the chemical adsorption. In MCFC it is possibly active oxide species ( $\text{O}_2^{2-}$  or  $\text{O}_2^-$ ) and adsorbing  $\text{CO}_2$  on surface of NiO that participate in the cathode reaction and form into carbonate ion. During the process of cathode reaction ( $P_{\text{CO}_2} > 0.1$  atm) the oxygen in crystal lattice of NiO and the adsorbing  $\text{CO}_2$  can form carbonate ion, and then enter molten carbonate. This will tend to result in the dissolution of nickel ion in NiO, namely, the dissolution and degradation of NiO material take place.

The in-situ Raman spectroscopic studies provide strong evidence for the  $\text{CO}_2$  adsorption. The desorption of  $\text{CO}_2$  occurred, however, only when Li/K carbonate and  $\text{O}_2$  atmosphere were present, as evident by the disappearance of the band of  $1090\text{ cm}^{-1}$  and the formation of a sharp band of  $1060\text{ cm}^{-1}$  at 923 K. Possible explanation for the role of carbonate and  $\text{O}_2$  played in the desorption of  $\text{CO}_2$  at NiO surfaces is that the active oxide species in molten carbonate (produced by reacting  $\text{O}_2$  with molten carbonate, such as  $\text{O}_2^{2-}$ ) could react with the adsorbing  $\text{CO}_2$  to form carbonate ions, which finally entered molten carbonate. And the lithiated NiO can be a site of electron-type transportation. Based on the experimental evidence, it can be concluded that at the cathode in MCFC the active oxide species ( $\text{O}_2^{2-}$  or  $\text{O}_2^-$ ) and adsorbing  $\text{CO}_2$  participate in reaction, while the lithiated NiO acts as the site of electron transportation. Hence it infers that during the process of cathode reaction ( $P_{\text{CO}_2} > 0.1$  atm) the loss of oxygen in crystal lattice of NiO material would take place by interacting strongly with adsorbing  $\text{CO}_2$  to produce  $\text{CO}_3^{2-}$ , which ultimately leads to the dissolution of nickel ion in NiO. Owing to the few opportunities to lose oxygen of crystal lattice, the dissolution of NiO material is a slow process.

It is noted that a severe shrinkage of the electrodes in Molten Carbonate Fuel Cell (MCFC) will result in a premature deterioration for MCFC system. The shrinkage of electrode resulted from the reduction of NiO cathode

thickness is considered to be a more pushed problem to be solved in MCFC exploitation.

A homemade LVDT displacement-measuring system (Fig.1) was set up and applied to study the process of deformation for the NiO in MCFC. A series of in-situ deformation tests were performed at a normal temperature ( $650\text{ }^\circ\text{C}$ ) of MCFC with porous Ni and NiO plaques under certain atmospheres and load condition in the presence of carbonate electrolyte. In the experiments the testing atmospheres were the mix gases of  $\text{CO}_2$ ,  $\text{O}_2$  and  $\text{N}_2$ , and the carbonate electrolyte was the Li/K eutectic carbonate with a ratio of 62:38. After in-situ deformation tests the post-experimental samples were analyzed by using XPS and SEM.

The experimental results indicated that the most significant deformation took place when Ni plaque underwent both in-situ oxidized and lithiated processes under a load condition, in particular, the deformation of Ni plaque occurred more severely at the beginning of processes. And the comparison and analysis from XPS and SEM results manifested that the deterioration of electrode materials was mainly due to its phase transformation under a load on the simulated conditions. Based on the experiments, it was inferable that quite a little certain component in electrode material dissolved in the molten carbonate and lost with its vapor when Ni transformed to lithium-doped NiO under a load, which might finally result in the severe deformation of the electrode materials.

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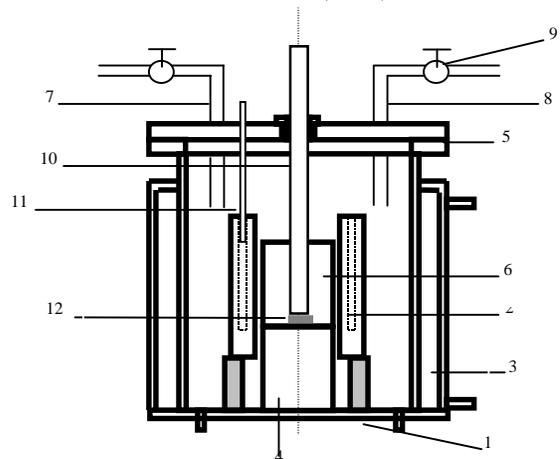


Fig.1 Detailed schematic diagram of vessel. 1.stainless steel vessel. 2.heater. 3.cooling system. 4.  $\text{Al}_2\text{O}_3$  supporter. 5.sealing cover. 6. $\text{Al}_2\text{O}_3$  crucible. 7.outlet. 8.inlet. 9.gas valve. 10.  $\text{Al}_2\text{O}_3$  load rod. 11.thermocouple. 12.sample.