$LiCoO_2$ coating on porous Ni plate by galvanic pulse plating method

B. H. Ryu*, J. Han, S. P. Yoon, S.W. Nam,
T.-H. Lim, S.-A. Hong, G. B. Kim*

Fuel Cell Research Center, KIST
P.O.BOX 131, Cheongryang, Seoul, Korea

*Dept. of Metallurgical Eng., Yonsei Univ.
134, Sinchon-dong Seodamun-gu, Seoul, Korea

NiO dissolution is considered as one of the major lifetime issues in molten carbonate fuel cell (MCFC) development. The dissolved Ni cations would be reduced by hydrogen from the anode side to form Ni precipitates eventually resulting in short-circuit in the matrix. In order to solve the problem of NiO dissolution, three approaches have been applied: the first one is to replace Li/K carbonate with Li/Na carbonate, because the higher basicity of Li/Na carbonate helps to suppress the NiO dissolution. The second one is to develop alternative cathode materials such as $LiCoO_2$ and $LiFeO_2$ which dissolve very little in molten carbonate electrolyte. The third one is to stabilize the conventional cathode by MgO addition or $LiCoO_2$ coating. The former is to increase the basicity of electrolytes and the latter is taking advantage of very low solubility of $LiCoO_2$ while avoiding the disadvantages of $LiCoO_2$ such as high cost and difficulty in enlargement. Even though the above-mentioned methods are able to reduce NiO dissolution to some extent, this problem can't be said to be completely resolved. Recently, many research efforts have focused on the development of $LiCoO_2$-coated cathode due to its comparable electrochemical activity with much less NiO solubility. However, the mechanism of suppressing NiO dissolution by $LiCoO_2$-coated cathode still requires more investigation. To verify the mechanism, it is necessary to have a well-prepared sample in terms of Co content and uniform distribution even inside the pores of cathode. Several methods such as sol-gel coating, solution coating and electroless plating, have been reported. But neither of them has been successful to make sample preparation easy and convenient

To solve this problem, the galvanic pulse plating method was employed to deposit $LiCoO_2$ and/or $Li_y(Co_x, Ni_{1-x})_{1-y}O_2$ on a porous Ni sheet in an aqueous solution. The process variables are pH of the bath solution, pulse on/off time, pulse current density and total plating time. Among them, pH of the bath solution, pulse 'On' time played the decisive role to determine the distribution of Co inside the pores. As seen in Figure 1, with increasing pH from 2 to 4, the porous Ni surface was covered with Co deposits, implying little penetration into the depth direction. Figure 2 verifyed the non-uniform distribution of Co when pH was 4. But when Ton time increased from 0.3 msec to 0.4 msec, Co could be distributed more uniformly. The XRD analysis in Figure 3 confirmed the presence of $LiCoO_2$ on the Ni surface after heat treatment at 450°C for 5 hours in air. The amount of Co could be easily controlled by adjusting the current density and total plating time. The distribution of Co stayed uniform until 12 wt. % of Co was deposited.

It was concluded that the galvanic pulse plating method could provide samples suitable for verifying the roles of Li and Co in suppressing NiO dissolution.

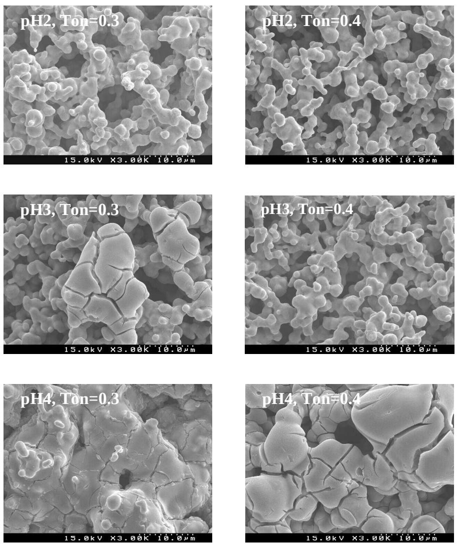

Fig. 1. Effect of bath solution pH on Co deposition (pulse current density=$100 mA/cm^2$)

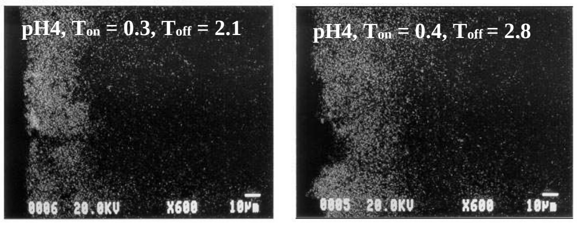

Fig. 2. Effect of pulse 'On' time (T_{on}) on distribution of Co inside the pores
(unit: msec)

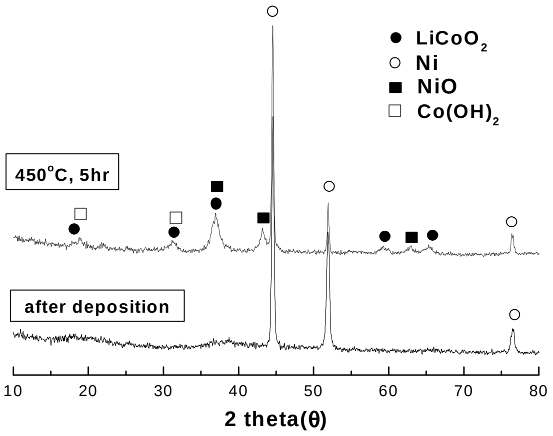

Fig. 3. Thin film XRD patterns of $LiCoO_2$ fabricated by galvanic pulse plating