In situ oxidation/lithiation and electrochemical behavior of NiCo alloy in molten Li/K eutectics

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Recently, CoO-NiO has been considered as one of the most promising cathode materials for MCFC. It is because CoO-NiO cathode showed relatively low NiO solubility in a molten carbonate. Thus, many research groups have elaborated intensive efforts to development of a fabrication process for CoO-NiO cathode and they have published many Co-coating processes, such as sol-gel and impregnation. However, very few studies have been reported on in situ oxidation and lithiation process of CoNi alloy, which is a green material for CoO-NiO cathode. Therefore, it is necessary to understand the oxidation and lithiation process in detail as well as the cathodic gas reaction on the CoO-NiO in molten eutectics in order to use such a solid solution as a cathode material in MCFC.

In the present work, the in situ oxidation and lithiation process of NiCo alloy with different cobalt contents were investigated in terms of crystal structure and electrochemical reaction. The NiCo alloy was prepared on gold foil by electroplating and EIS test was carried out in molten $(Li_{0.62}K_{0.38})_2CO_3$ at 923K using $Au\,|\,0.33\ O_2 + 0.67\ CO_2$ gas reference electrode (SOR). As shown in Figure 1, the OCP variation with immersion time of Ni and NiCo alloy in molten eutectics can be divided into three stages; oxidation of the metals (stage I), lithiation (stage II) and oxygen reduction (stage II). Although the shapes of the OCP variation of Ni and CoNi were similar, CoNi alloy stayed longer at stage I than Ni and the period of stage I was getting longer with Co contents in CoNi alloy. The lattice parameters evaluated from the XRD results were plotted in Figure 2 with immersion time. Lattice parameters increased at the oxidation stage and then decreased with increasing immersion time from stage II. Its maximum values, regardless to Co contents, were interestingly found at the potential range from -0.45V to -0.3V vs. SOR, which was located at the stage II. In addition, the lattice parameter of the NiCo alloys with higher Co content varied in wide range. It means that NiCo alloys with higher Co content showed higher maximum value at stage II and lower value at stage III. Therefore, it was clear that the lattice parameters increased at oxidation process and the reduction of lattice parameters with immersion time was related to lithium incorporation. Accordingly, it could be concluded that similar to Ni, NiCo was oxidized in the first stage of immersion and then was lithiated. The phase transformation of oxidized NiCo alloy due to lithium incorporation depended on the composition of solid solution.

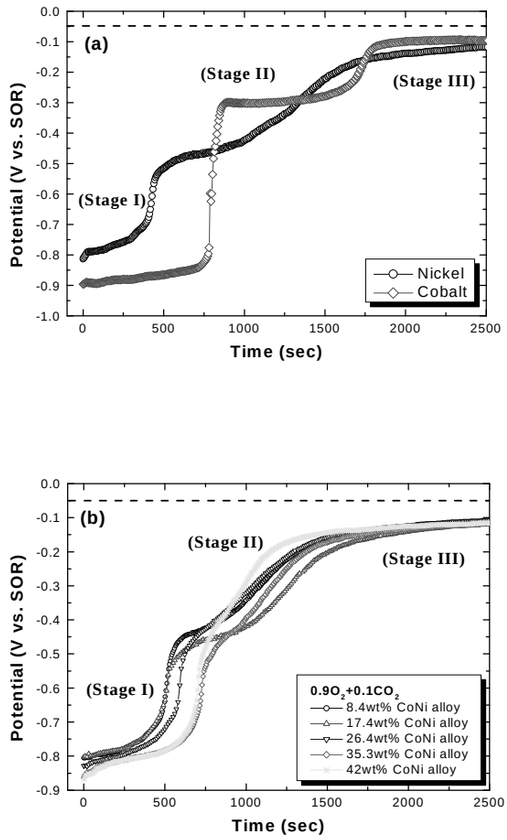

Fig. 1. Variation of open circuit potential of Ni and NiCo ally in molten Li/K eutectics at 923K. (a) Ni/Au, (b) NiCo alloy/Au, the thickness of deposited layer is ca. 4μm

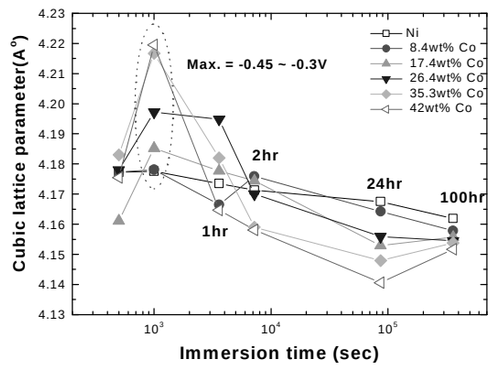

Fig. 2. Variation of cubic lattice parameter of Ni and NiCo alloy during oxidation and lithiation process.