$LiFeO_2$-$LiCoO_2$-NiO Cathodes for Molten Carbonate Fuel Cell (MCFC)

Athula Wijayasinghe[a], Bill Bergman[a], Carina Lagergren[b] and Anders Eriksson[a]

[a]Department of Materials Science and Engineering, and [b]Department of Chemical Engineering and Technology, KTH (Royal Institute of Technology), SE-100 44 Stockholm, Sweden

Dissolution of the state-of-the-art lithiated nickel oxide cathode is a major obstacle for the development of MCFC technology (1). Alternative cathode materials should be selected on the basis of their chemical, thermal and morphological stability as well as possessing adequate electronic conductivity. $LiFeO_2$ and $LiCoO_2$ (2-4) have so far been reported as the most prominent alternative materials, however, they could not satisfactorily substitute the state-of-the-art cathode. A solid solution consisting of $LiFeO_2$, $LiCoO_2$ and NiO is expected to posses some of the desirable properties of these three materials (5). The aim of this research work was to find alternative cathode materials in the $LiFeO_2$-$LiCoO_2$-NiO system by investigating electronic conductivity of the materials and evaluating their electrochemical performance.

Pechini and Glycine-nitrate processes were used for powder preparation followed by calcination to complete the reaction. Nitrogen adsorption method, Pycnometry, X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) were employed for powder characterization. D.C. electrical characterization by four-probe method was performed on pellets. Selected compositions were tape-cast and sintered to obtain porous-gas-diffusion cathodes. SEM and XRD were employed for mictrostructural characterization and phase analysis of prepared cathodes. Pore size distribution was obtained by mercury porosimetry and d.c. electrical conductivity by van der Pauw technique. The porous cathodes were characterized electrochemically in a laboratory-scale fuel cell of 3 cm^2 area. Performance of cathodes has mainly been studied by steady–state polarization curves obtained under different conditions. The electrolyte consists of an eutectic mixture of 62 mol% Li_2CO_3 and 38 mol% K_2CO_3 and the experiments were performed under optimal degree of electrolyte fill. Tests have been performed with standard gases of 15/30/55% $O_2/CO_2/N_2$ and 80/20% H_2/CO_2 humidified at 60°C for the cathode and the anode respectively and varying the temperature. The obtained potentials were corrected for the ohmic drop in the cell.

Fig.1 shows the details of the prepared compositions. Initially, the binary compositions were subjected to preliminary characterizations. A continuous range of solid solution was observed in the $LiFeO_2$-NiO binary system, however, some multi-phase materials were detected in other binary systems (5). It also revealed the existence of single-phase materials, possessing adequate electrical conductivity, with $LiFeO_2$ content higher than 10 mol%. A study on the ternary system, with constant 1:1 ratio of $LiFeO_2$:NiO but varying the content of $LiCoO_2$, revealed the existence of a solid solution up to 10 mol% of $LiCoO_2$. Fig.2 shows the d.c. electrical conductivity of these compositions. Based upon them, some of the compositions were subjected to electrochemical performance studies. Preliminary measurements on the cathode performance in the operating fuel cell showed promising results.

References

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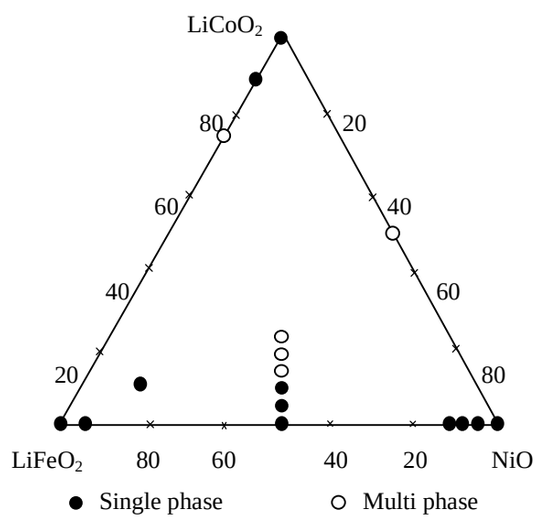

Fig.1 Compositions in the $LiFeO_2$-$LiCoO_2$-NiO system

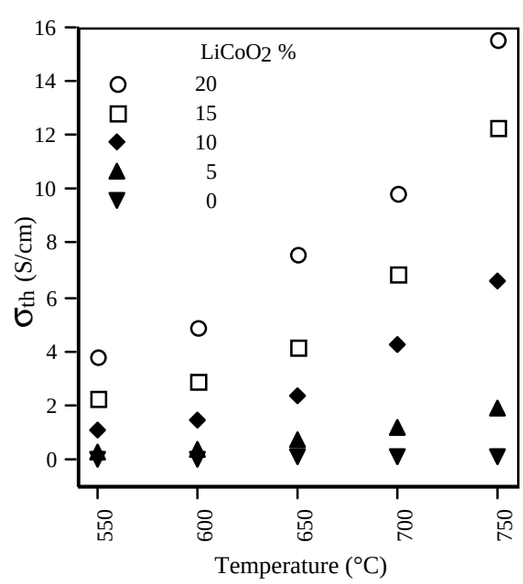

Fig.2. D.C. electrical conductivity (at theoretical density) in cathode gas environment of the compositions prepared by varying the content of $LiCoO_2$ while keeping $LiFeO_2$: NiO ratio as 1:1.