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Report Title

Fabrication and Evaluation of MC Modified Cathode in SOFCs

ABSTRACT

Recent progress on the experimental research of the project "Theoretical Design and Experimental Evaluation of Molten Carbonate Modified LSM Cathode for Low Temperature Solid Oxide Fuel Cells".

Theoretical Design and Experimental Evaluation of Molten Carbonate Modified LSM Cathode for Low Temperature Solid Oxide Fuel Cells

[Experimental Research Progress Report]

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Preparation of LSGM electrolyte

The $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}$ (LSGM) powder was prepared by conventional solid state reaction. La_2O_3 (99.9% purity, Alfa Aesar), SrCO_3 (99.9% purity, Alfa Aesar), Ga_2O_3 (99.9% purity, GFI) and MgO (99.9%, Alfa Aesar) were used as starting materials. Prior to weighing, La_2O_3 and MgO were calcined at 1000 °C for 5 h to remove non-oxide components. Stoichiometric amount of these materials were weighed and then mixed with acetone in an agate mortar. The raw powder was pressed and subsequently fired at 1250 °C for 10h. The pre-calcined samples were ball milled to obtain raw LSGM powder.

The LSGM electrolyte was prepared by standard tape casting method. The slurry formulation consisted of 5.5 g Terpineol (Aldrich) as solvent; 0.05 g Hypermer (Croda) as dispersant; 9.5 g LSGM powder; 0.5 g Ethyl cellulose as binder; 0.5 g Dioctyl phthalate (Acros) as plasticizer. After these components were mixed and ball milled, the slurry was vacuumed to remove air. The slip was then casted onto a silicone-coated Mylar with a tape casting machine (TTC-1200, Richard E, Mistler, Inc.). After dried at 80 °C for 5 h, the tape was cut into $\phi 20$ mm circles and fired at 1450 °C for 5h. The finally sintered LSGM electrolyte thick films were 15 mm in diameter and 200-250 μm in thickness.

Fabrication of symmetric cell and infiltration of molten carbonate

Commercial LSM powder (Nextech) was used as the cathode material. The powder was made into a paste by grinding with organic binder (V-006, Heraeus). The paste was screen printed on both sides of LSGM pellets and fired at 1100 °C for 2 h.

Li-K binary eutectic salts were prepared for infiltration. Li_2CO_3 (99%, Alfa Aesar) and K_2CO_3 (99%, Alfa Aesar) were mixed with a molar ratio of 62:38 and heated at 650 °C for 2 h to form a eutectic melt. In addition, eutectic melts containing 0.5 mol % La_2O_3 (99.9%, Alfa Aesar) or 0.5 mol % Gd_2O_3 (99.9%, Alfa Aesar) were also prepared. For infiltration, the eutectic melt was ultrasonic dispersed in ethanol. A few drops of the salt suspension were dripped on the surface of LSM cathodes and dried at 100 °C. This step was repeated till 5 mg salt was added. The samples were then heated to 650 °C in air for 2 h.

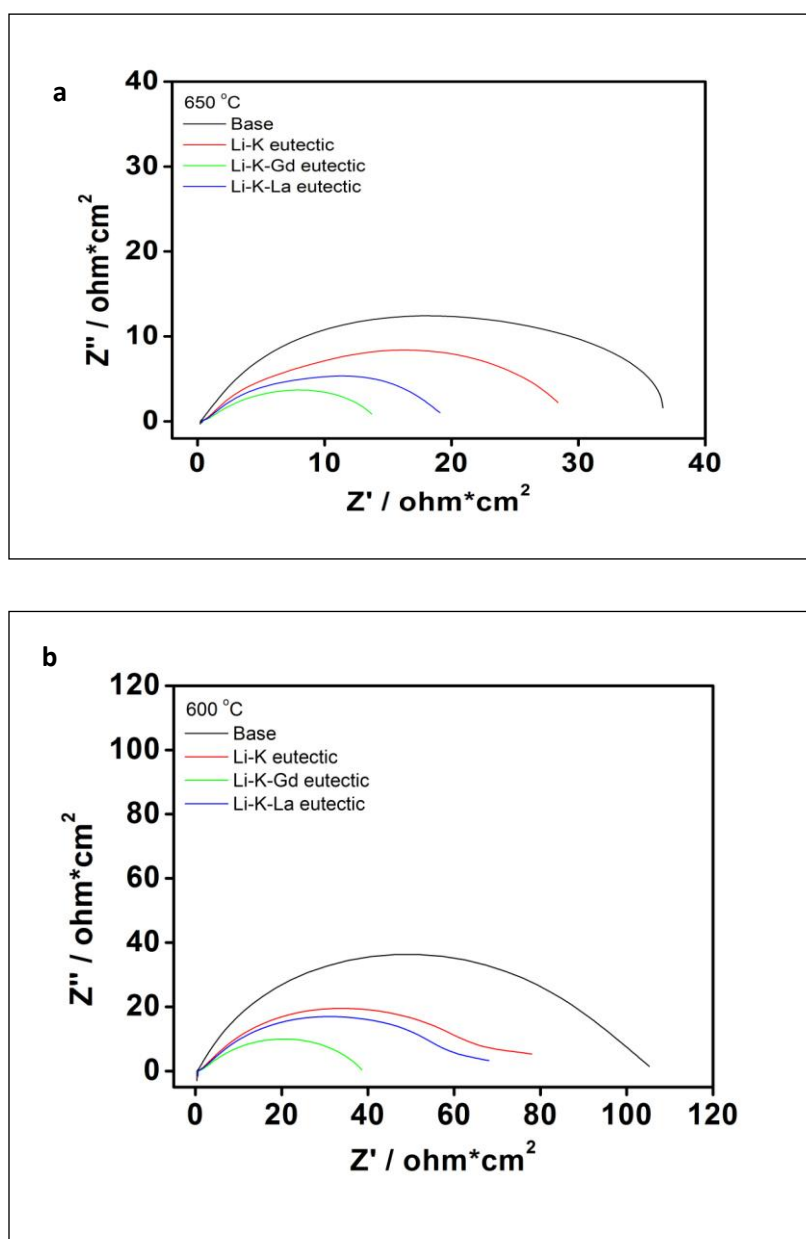
Electrochemical test

Silver mesh was attached to the LSM cathode using silver paste (C8829, Heraeus) for current collecting. Electrochemical Impedance Spectroscopy (EIS) of the symmetrical cells was obtained with an electrochemical workstation (IM6, Zahner) under open circuit conditions from 500 to 650 °C with 50 °C interval. The frequency range was swept from 10^5 to 0.05 Hz with an AC amplitude of 20 mV. EIS

spectra were simulated and fit with Thale equivalent circuit software (Zahner). The electrode polarization was taken from the two intersections of the spectrum at the highest and lowest frequencies. Thus obtained polarization resistance was then divided by two and corrected for the cathode area to arrive at the actual area-specific resistance of the cathode polarization.

Results and discussion

Fig.1 (a)-(d) shows the polarization resistances of LSM cathode without (baseline) and with eutectic carbonate melts from 500 to 650 °C. The baseline LSM sample exhibits the largest polarization resistance. After infiltrated with 5 mg eutectic melts, polarization resistance has been decreased significantly. Addition of rare earth oxides La_2O_3 and Gd_2O_3 further improved the kinetics of oxygen reduction reaction. Among all the tested samples, Gd_2O_3 -added Li-K carbonate melt shows the lowest area specific resistance (ASR), a 57% reduction at 650 °C and 80% at 500 °C compared to the baseline.



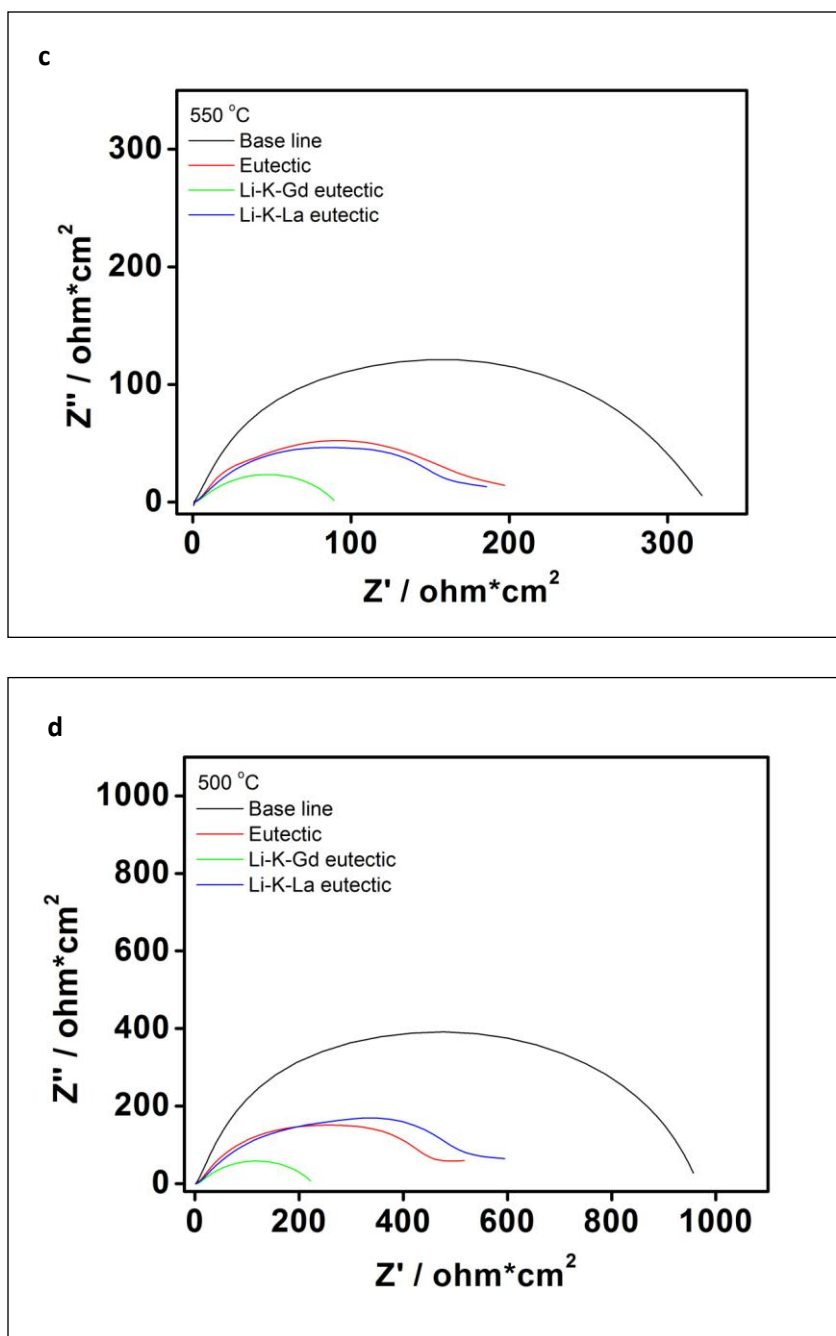


Fig.1: Area-specific resistance of LSM cathode polarization without and with eutectic carbonate melts measured at different temperatures.

Fig.2 shows the Arrhenius plot of cathode polarization for base and eutectic melt-infiltrated LSM samples. Introduction of eutectic melts into the porous LSM cathode effectively lower the activation energy, suggesting that eutectic carbonate melts can promote the kinetics of oxygen reduction reaction.

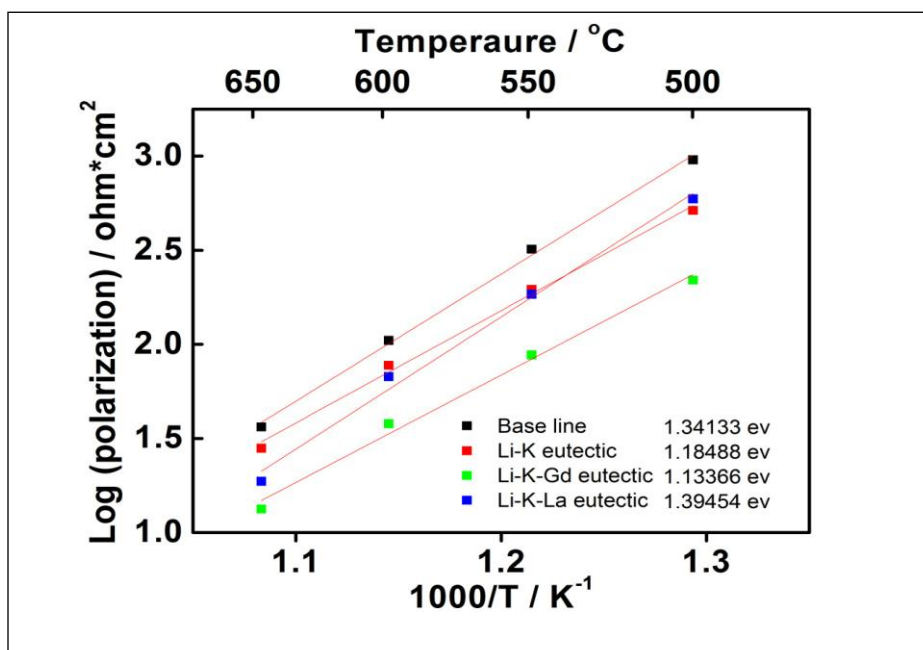


Fig.2: Temperature dependence of area-specific polarization resistance for the baseline and eutectic melt-infiltrated LSM cathode from 500 to 650 °C.

Conclusion

From the reported initial results, we can conclude: (1) Molten carbonate can improve the efficiency of LSM cathode by 50% in SOFCs; (2) Addition of MC to LSM can reduce the activation energy of oxygen reduction in the cathode of SOFCs; (3) Rare earth oxides La_2O_3 and Gd_2O_3 can also improve the cathode performance. However, the experiments could not provide any details on the fundamental steps relative to the enhancement mechanism. On the other hand, the theoretical team already proposed an oxygen reduction mechanism through CO_4^{2-} intermediate and this should be verified by experiments in the coming year.

Future Work

For the experimental side, the research will be geared to fundamental steps in the ORR process with the presence of MC. If combined with DFT results, those experimental data will give a better understanding of ORR and also will confirm the theoretical work. More specifically, the spectroscopic study of reaction intermediates and diffusion of oxygen species in MC will be examined. Those should also be investigated under the cell running conditions.