Reversible Ageing Behavior of LSM Electrodes at Open Circuit

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Introduction:
LSM remains one of the most popular cathode materials in solid oxide fuel cells because of its long-term stability. We describe here an ageing behavior of LSM electrodes which has not, to our knowledge, been reported in the literature. Symmetrical cells with LSM electrodes and YSZ electrolyte were held at 700, 750, 800 and 850°C in air and characterized periodically with cyclic voltammetry and electrochemical impedance spectroscopy to monitor the polarization resistance. The cells remained at open circuit between measurements. Initially, there were irreversible changes in the polarization resistance, most commonly a brief rise and then a significant decay in the polarization resistance. The rate of change increased with the temperature. After the initial conditioning of the cell, the polarization resistance showed a reproducible rise in polarization resistance at 700°C, and a reproducible decay in polarization resistance at 800°C, with the temperature being changed every 2-3 days.

Discussion
There is considerable discussion in the literature concerning the sharp decrease in polarization resistance of LSM cathodes during the initial application of current. Of the many possible mechanisms, we favor migration of strontium within LSM material (e.g., cracking, de-wetting). Samples of LSM are being analyzed to check for changes in cation surface compositions as a function of thermal history of the LSM electrodes.

Fig. 1. NexTech Hionic™ electrolyte-supported cell with LSM/GDC composite cathode.
A. Impedance plots during ageing at 750°C.
B. Impedance plots during ageing at 850°C.

Fig. 2. Initial polarization resistance changes at 700°C and 850°C during temperature cycles (Fig 2 depicts Rp (ohms cm2) for a LSM/YSZ/LSM symmetrical cell.

Fig. 3. Polarization resistances of the cell in Fig. 2 at (a) 700°C and (b) 800°C during temperature cycles. A. Impedance plots during ageing at 700°C, B. Impedance plots during ageing at 850°C.

Fig. 4. Polarization resistances of LSM/YSZ symmetrical cells soaked at (A) 700°C or (B) 800°C for 500 hours.

Fig. 5. Polarization resistances of Cell A above during temperature cycles at (a) 700°C and (b) 800°C.

Fig. 6. Polarization resistances of the cell in Fig. 4B during temperature cycles at (a) 700°C and (b) 800°C.

Primary Observations
1) Evolution of polarization resistance over 40+ hour periods is controlled by at least 2 processes (Fig 2 depicts Rp maximum).
2) A reversible change in polarization resistance occurs over 40+ hour thermal cycles from 700 to 800°C (Fig 3, Fig 5, Fig 6).
3) The repeatability of the reversible change depends on the cell thermal history (Compare Fig 5 and Fig 6), indicating the existence of an irreversible process.

Fig. 5. Polarization resistances of Cell A above during temperature cycles at (a) 700°C, and (b) 800°C.

Fig. 6. Polarization resistances of the cell in Fig. 4B during temperature cycles at (a) 700°C and (b) 800°C.

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There is considerable discussion in the literature concerning the sharp decrease in polarization resistance of LSM cathodes during the initial application of current. Of the many possible mechanisms, we favor migration of strontium within LSM phase as the cause of the reversible changes in polarization resistance. Strontium segregation (with possible formation of a new phase) is favored at 700°C, while migration of strontium into the bulk occurs at 800°C. The irreversible changes in polarization resistance may be a combination of the cation migration and structural changes in the LSM material (e.g., cracking, de-wetting). Samples of LSM are being analyzed to check for changes in cation surface compositions as a function of thermal history of the LSM electrodes.

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