Nanoparticles Infiltration in Air Electrode of LSM-YSZ/YSZ/Ni-YSZ Cells to Improve Performance and Mitigate Performance Degradation under Reversible SOFC/SOEC Operation

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Introduction

- Shares of renewable energy of solar and wind energy are expected to increase from 25% in 2018 to more than 40% by 2040 in order to reduce dependency on fossil fuels and mitigate greenhouse gas emissions.[1]
- Keeping electric grids balanced for supply and demand, especially for smaller or more isolated sections of grids with a larger share of intermittent renewable energy systems, is a significant challenge. Wind and solar energy supply strongly depend on weather patterns with intermittent and fluctuating features.[2]
- Developing energy storage systems to balance electricity production and consumption is critical to reduce stress on the energy grid and to increase the share of renewable energy.
- Reversible solid oxide fuel cell and solid oxide electrolysis cell (r-SOFC/SOEC) systems capable of both SOFC mode for power generation and SOEC mode for achieving energy storage within one reactor received widespread attention for the potential of being a cost effective, highly efficient and promising electrical energy storage technology[3-5] in multi-energy distributed systems.
- Application of a r-SOFC/SOEC system in the energy grid will be challenged for its long-term stability since r-SOFC/SOEC operation involves both SOFC and SOEC operation, for which performance degradation may be worse.
- Infiltration of nanoparticles in the O_2 and H_2 electrode has been proven to be important in the development of high-performing electrodes, giving them suitable microstructure for oxygen reduction or fuel oxidation. Infiltration enhances the catalytic activity via fine-dispersed nanoparticles and increases ionic and/or electronic conductivity via connected particles of fuel cell electrodes, leading to cell power boost.

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3. Paolo Di Giorgio and Umberto Desideri, Potential of Reversible Solid Oxide Cells as Electricity Storage System, Energies 2016, 9, 662.
4. Guo-Bin Jung, Chang-Tsair Chang, Chia-Chen Yeh, Xuan-Vien Nguyen, Shih-Hung Chan, Cheng-You Lin, International Journal of Hydrogen Energy 41 (2016) 21802-21811.
5. Yuqing Wang, Aayan Banerjee, Lukas Wehrle, Yixiang Shi, Nigel Brandon, Olaf Deutschmann, Energy Conversion and Management 196 (2019) 484–496.

Purpose of the Study

- Mitigate performance degradation and delamination of the air electrode from electrolyte for LSM/YSZ cell operated under r-SOFC/SOEC by infiltration of Sr-Fe-O in the air electrode of the LSM/YSZ cell.
- Evaluate nanostructure of Sr-Fe-O infiltrated LSM/YSZ cell before and after long-term test through TEM/HRTEM studies and analysis.
- Gauge improved performance and performance stability of Sr-Fe-O infiltrated cells.

Experimental Methods

Commercially available Nexceris cells were used in this study:

- Air electrode: LSM[(La0.8Sr0.2)0.98MnO3] / LSM-YSZ active layer
- Electrolyte: YSZ
- Fuel electrode: Ni-YSZ

Infiltration of nanomaterials in LSM/YSZ cells:

- Infiltrated nanomaterials: Sr-Fe-O
- Particle size: 50–100 nm
- Solvent: aqueous citric acid solution
- Chemical precursors: metal nitrate (0.125 – 0.25 M)
- Temperature: 450–850 °C
- Time: repeat infiltration until 0.3–0.7 mg infiltration obtained

Operating Conditions:

- SOFC operational mode: 800 °C, 0.5 A/cm² current load, dry H_2
- SOEC operational mode: 800 °C, 0.5 A/cm² current load, 60% steam in H_2 electrode

TEM/HRTEM studies and analysis:

- Nanostructure changes of Sr-Fe-O infiltrated cell before and after test by TEM/HRTEM

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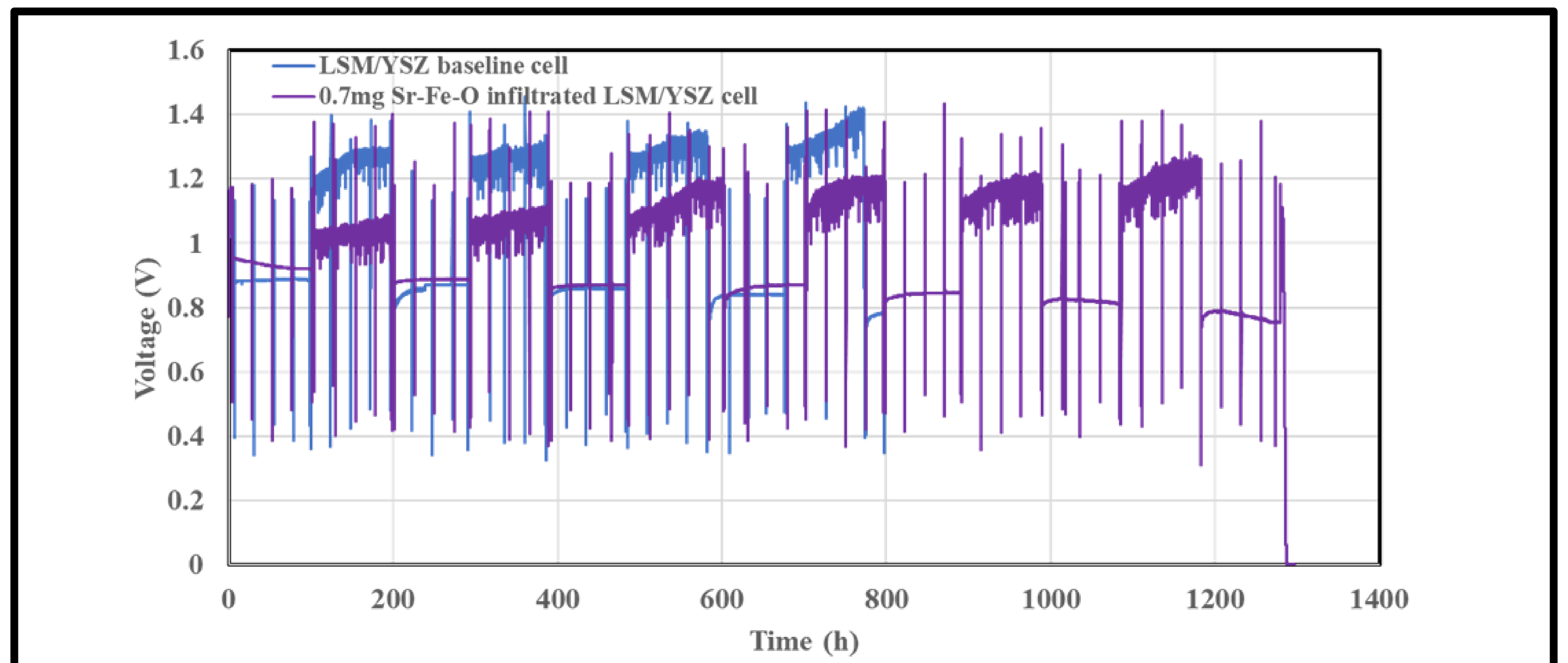
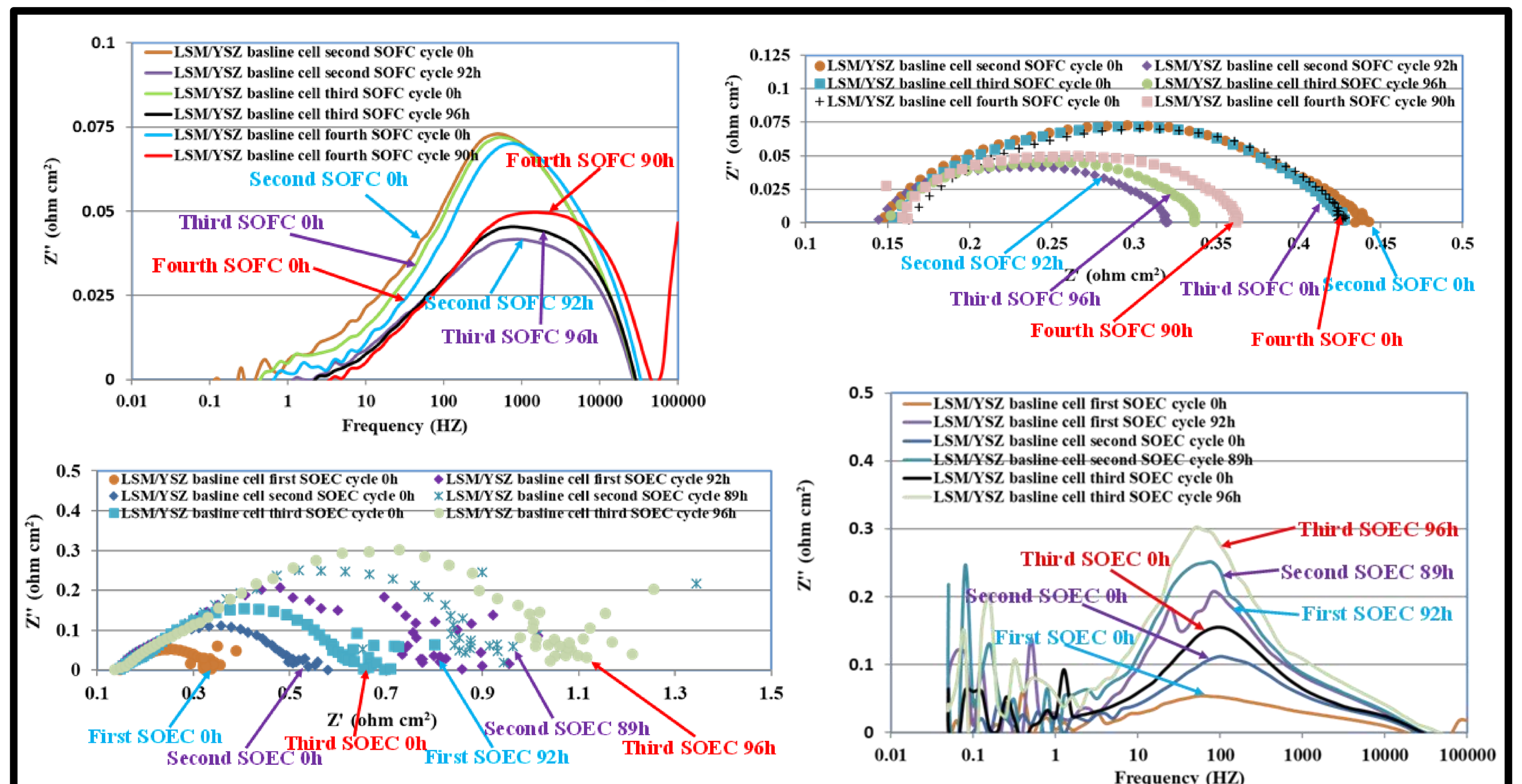
Stability Tests of Uninfiltrated and Sr-Fe-O Infiltrated LSM/YSZ Cells Under Reversible SOFC/SOEC Operational Mode



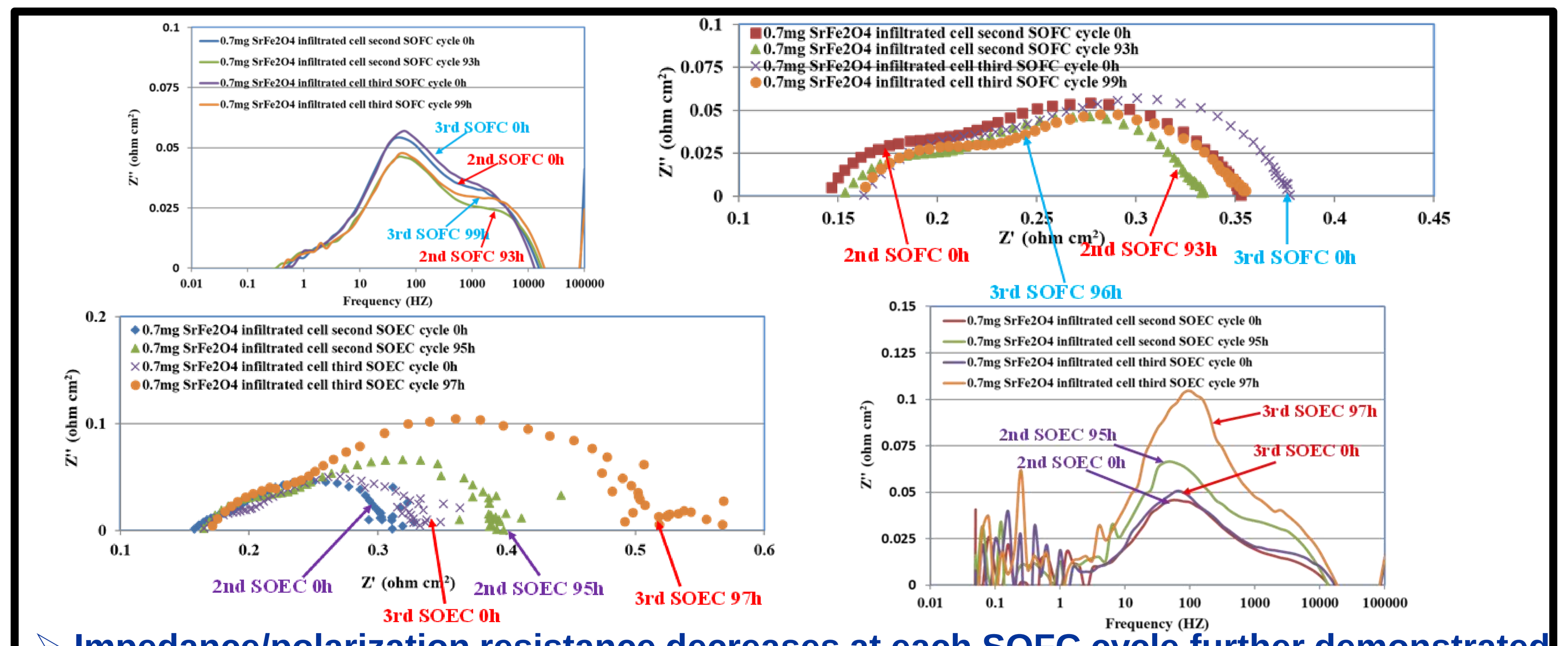
- LSM/YSZ baseline cell's performance degraded by 11.6% after four cycles of reversible SOFC/SOEC operation. The LSM/YSZ baseline cell air electrode delaminated from the electrolyte after only four cycles of r-SOFC/SOEC operation.
- Sr-Fe-O infiltrated cell performance degraded by 8.9% after four cycles of r-SOFC/SOEC operation, primarily due to degradation in the first SOFC cycle. Performance of the Sr-Fe-O infiltrated cell degraded by 17.5% after six cycles of r-SOFC/SOEC operation.
- Sr-Fe-O infiltrated cell showed no visible delamination in the air electrode after six cycles of r-SOFC/SOEC operation. Sr-Fe-O infiltration in the air electrode significantly improved the cell's performance for the SOEC cycle and extended r-SOFC/SOEC cycle operational duration without air electrode delamination.

EIS Studies of Uninfiltrated LSM/YSZ Baseline Cell under r-SOFC/SOEC Operation



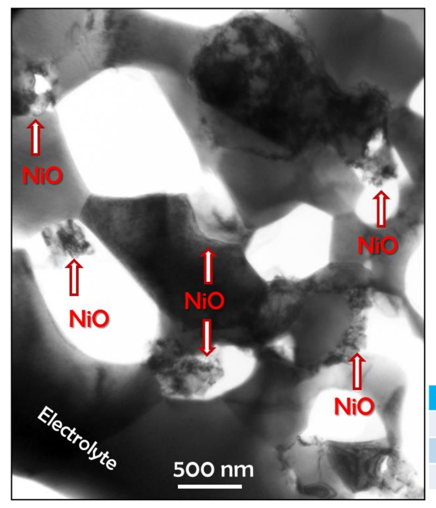
- Impedance/polarization resistance of each SOFC cycle at 0 h were higher than the last SOFC cycle at 96 h, which denoted that the SOEC cycle contributed most to performance degradation.
- Impedance/polarization resistance of each SOEC cycle at 0 h was significantly lower than the last SOEC cycle at 96 h, which demonstrated that an SOFC cycle recovered part of the performance loss suffered during the prior SOEC cycle.
- Performance degradation mainly occurred in SOEC cycles, corresponding to the voltage increase during SOEC cycle operation in the voltage-time plot.
- With continued r-SOFC/SOEC cycle operation, impedance/polarization resistance increased, contributing to performance degradation.

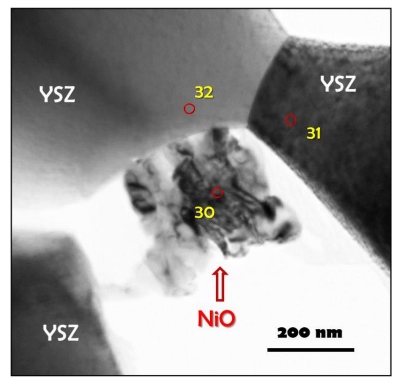
EIS Studies of Sr-Fe-O Infiltrated LSM/YSZ Cell Operated under Reversible SOFC/SOEC



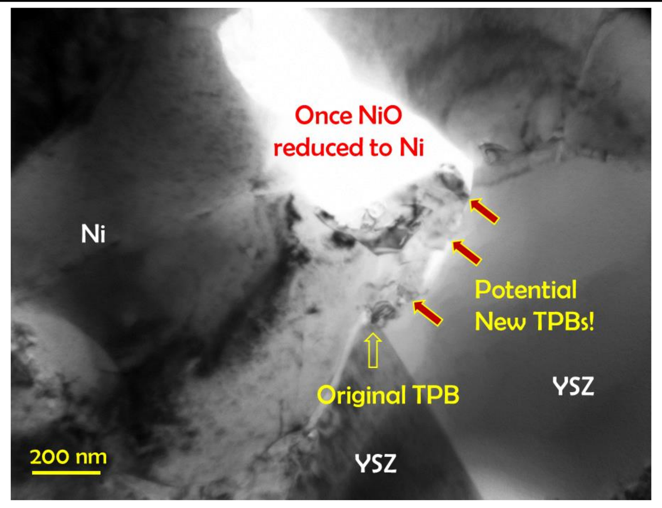
- Impedance/polarization resistance decreases at each SOFC cycle further demonstrated that SOFC cycles recovered some performance loss caused by SOEC cycles.
- Impedance/polarization resistance of each SOFC cycle at 0h were higher than that of last SOFC cycle at 96h, which indicates the cell's performance degradation was mainly caused by the SOEC cycle.
- Impedance/polarization resistance of each SOEC cycle at 0h were less than that of last SOEC cycle at 96h, which further indicated that SOFC cycle operation recovered some part of performance loss from SOEC cycle operation.
- Impedance/polarization resistance of each SOEC cycle increased substantially, which denoted that performance degradation mainly occurred during SOEC cycles.

TEM Studies on H_2 Electrode for Uninfiltrated LSM/YSZ Baseline Cell Operated Under Reversible SOFC/SOEC





At %	O	Zr	Y	Ni	Formula
30	61.90			38.10	NiOx
31	45.69	46.42	7.89		$Zr_{0.85}Y_{0.15}Ox$
32	56.20	36.75	7.06		$Zr_{0.84}Y_{0.16}Ox$



- A large number of NiO clusters relocated into the original pore region. Ni migration manifested by the formation of secondary phases of NiO at the original pore region.
- NiO relocation occurs at the YSZ surface.
- If NiO is reduced to Ni, Ni migration could temporarily result in the addition of new TPBs for SOFC operation. NiO formed in the H_2 electrode of uninfiltrated and infiltrated cells during SOEC operational cycle subsequently reduced to Ni during SOFC cycle which may explain recovered performance.

Summary & Conclusion

- Overall cell performance degradation of both uninfiltrated and infiltrated LSM/YSZ cells was mainly attributed to SOEC cycle operation.
- SOFC cycles recovered some performance loss caused by SOEC cycle operation. Most of the performance loss during a prior SOEC cycle was recovered at 24h of SOFC operation.
- NiO formation in the H_2 electrode during a SOEC operational cycle could cause cell performance degradation. NiO reduced to Ni during a subsequent SOFC cycle which may explain recovered performance during a SOFC cycle.
- Infiltration of Sr-Fe-O in the air electrode of the LSM/YSZ cell mitigated performance degradation and prevented delamination of the air electrode from the electrolyte.