Microstructure Tailoring of Infiltrated Cathode to Control Activity and Stability

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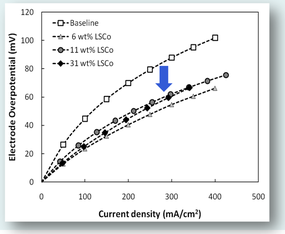
Prior work: Cathode Activation by Electrocatalyst Infiltration

- **Dramatic reduction in electrode overpotential due to enhanced oxygen reduction reaction rate.**

* **Shiwoo Lee et al., J. Electrochem. Soc., 158 (2011) B735.**



Motivation of current work

1. New electrocatalyst: Noble Metal (Pt)-substituted Perovskite (LSCo)

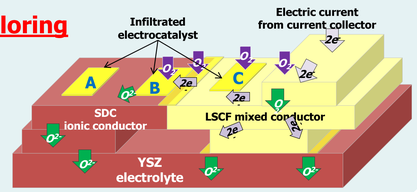
Solid-solution of noble metal with perovskite oxides is expected to
(1) prevent the metal's irreversible coarsening (agglomeration),
(2) reduce losses due to volatilization at high operating temperatures, and
(3) avoid reactions with other components that lead to catalyst deactivation.

2. Demonstration: Microstructure tailoring

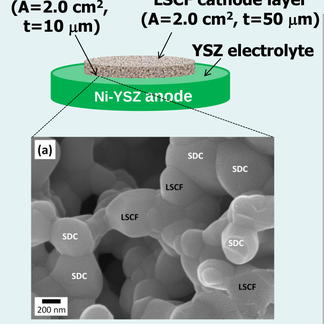
Solution chemistry

Microstructure of cathode

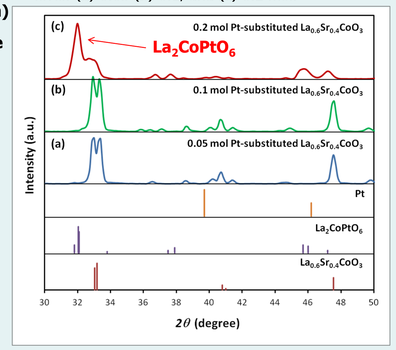
Cell performance



Experimental



X-ray diffraction patterns of Pt-substituted LSCo calcined at 850°C for 4 h with different Pt doping level: (a) 0.05 (b) 0.1, and (c) 0.2 mol.



- Precursor of infiltration solution

	Material
Metal precursors	Nitrates of La, Sr, Co, and Pt
Polymeric additives	Citric acid Ethylene glycol
Solvent	Water / Ethanol / Mixed solvent

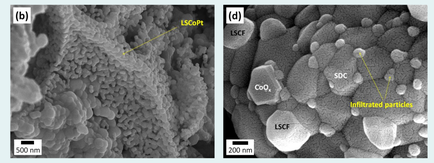
(1) Polymerization complex (PC) route

Step 1: Complexation of metal ions with citric acid

Step 2: Polymerization, where the formed chelates undergo polyesterification with a polyhydroxyalcohol (Ethylene glycol)

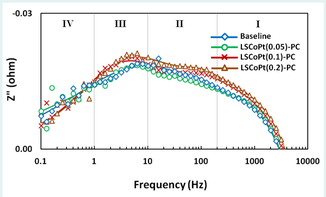
Step 3: Decomposition of the formed organic network leaving porous ceramic structure.

SEM images of the cathode functional layer of the cell infiltrated with 20 wt% LSCoPt-PC, subsequently calcined at 850°C, and tested at 750°C for 200 h. .



- **Clusters** of infiltrated particles with well-developed **porous network structure** are formed. The surface of the cluster is smooth and concave: It is assumed to be formed by **delamination** during calcination process.
- Infiltrated particles of >100 nm in size show a tendency of **discretely positioning** at the **triple junctions of SDC grains**. It would be originated from **high surface tension** of the infiltration solution containing Pt precursor, which ultimately induces higher contact angle of the infiltrates to the backbone grains.

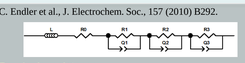
Bode plots of a baseline cell and the cells infiltrated with LSCoPt precursor of different Pt doping level; 0.05, 0.1, and 0.2 mol of B-site stoichiometry, with citric acid and ethylene glycol (LSCoPt-PC).



Impedance spectra were almost invariant after infiltration of LSCoPt-PC.
⇒ **No evidence of activation by infiltration**

- Data were obtained under DC bias of 0.5 A/cm² after 24 h operation at 750°C. Solid lines are the data fitted to an equivalent circuit model.

Ref) C. Endler et al., J. Electrochem. Soc., 157 (2010) B292.



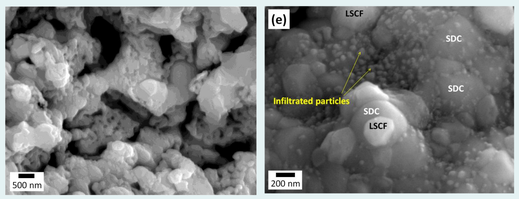
(1) R_Ω: ohmic resistance
(2) R1Q1 (Region I), > 150 Hz: Charge transfer/bulk diffusion
(3) R2Q2 (Region II), 10 - 150 Hz: surface oxygen exchange reaction at cathode
(4) R3Q3 (Region III), 1 - 10 Hz: Concentration polarization of anode
(5) < 10^0 Hz: Concentration polarization of cathode

(2) Non-PC route (NPC)

Non-Polymerizable complex route:

Precursor solution composition:
Nitrate of La, Sr, Co, and Pt + citric acid (**w/o ethylene glycol**)

SEM image of the composite cathode infiltrated with aqueous solution unsupplied with ethylene glycol **(LSCoPt-NPC)** followed by calcinations at 850 C and operation at 750 C for 280 h.

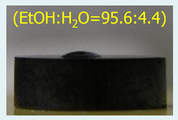


Removal of ethylene glycol and resultant non-polymerizable complexing process made infiltrated particles much smaller in size (~ 50 nm) free of macro-network structure.

(3) Mixed solvent (MS)

Water-based solution

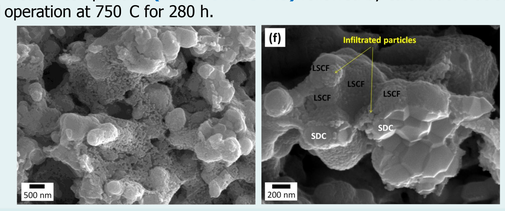
Mixed solvent solution (EtOH:H_2O=95.6:4.4)



Issue with insolubility :$Sr(NO_3)_2$ in EtOH

2-step Infiltration
1) La, Co, Pt in mixed solvent
2) Sr in H_2O

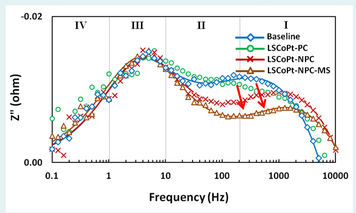
SEM images of the cathode infiltrated with mixed solvents, ethanol and water, of the same composition **(LSCoPt-NPC-MS)** followed by calcinations at 850 C and operation at 750 C for 280 h.



Numerous fine infiltrate particulates are observed to coat surfaces of backbone grains homogeneously, possibly due to **reduced surface tension** of infiltration solution of mixed solvent. Combination of non-polymerizable complexing route (NPC) and lower surface tension of the solution (MS) is believed to produce very fine infiltrates that are nearly continuous over the entire composite cathode.

Effects on cell performance

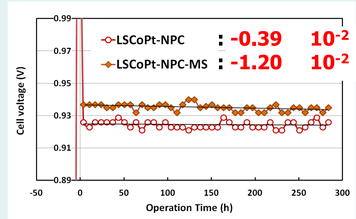
Bode plots of a baseline cell, cell LSCoPt-PC and the cells infiltrated with LSCoPt precursor of modified compositions (LSCoPt-NPC and LSCoPt-NPC-MS).



Impedance of **region II (10-200 Hz) is reduced** for the cells **LSCoPt-NPC** and **LCoPt-NPC-MS**:

⇒ **Clear evidence of cathode activation by infiltration**

Cell voltage vs. operation time of the modified cells under the constant current of 0.25 A/cm² at 750°C.



Conclusion

- Microstructure and electrochemical performance of commercially available SDC-LSCF composite cathode infiltrated with $La_{0.6}Sr_{0.4}Co_{1-x}\mathbf{Pt_x}O_3$ was investigated.
- **Modification** of polymeric additives and solvent **exerted critical influence** on nanostructure of infiltrated cathode and, ultimately, cell performance.
- **The cells infiltrated with the modified solution system showed enhanced cathode activity and exceptional stability for 280 hours**.
- Additional mechanistic understanding and microstructural scrutiny will allow further control over activity and stability of infiltrated cathode systems.

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