Low-Temperature Electronic Conductivity in Cu-doped CeO_2 Nanoparticles

Syed Saam Rasool, Yanhe Li, Siu-Wai Chan[1]

[1]Department of Applied Physics & Mathematics (Materials Science & Engineering), Columbia University, New York, NY

SENIOR DESIGN '23 EXP

Motivation

Cerium oxide, or ceria, (CeO_2) is a ceramic material with noteworthy electronic properties. Doping this material with copper has shown to be useful in the catalysis of several reactions, including the high-temperature reverse water gas shift reaction, and as a component in solid oxide fuel cells. In this project, we synthesize nanoparticles of copper-doped ceria (Cu-CeO_2) and measure their conductivity using electrochemical impedance spectroscopy (EIS).

Background

Two mechanisms of electronic conduction have been hypothesized to occur in cerium oxide. At high temperatures, positively-charged oxygen vacancies formed by aliovalent doping or intrinsic Schottky defects can diffuse through the solid. At low temperatures, small polarons (distortions in the lattice caused by an extra electron in the 4f orbital) are mobile due to activation by optical phonons. At the temperatures measured in this experiment, the latter is most likely responsible for the conductivity observed.

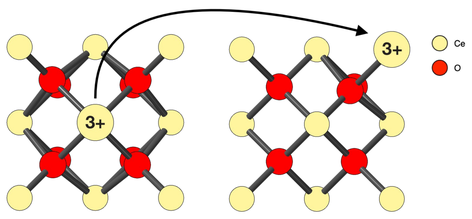

Fig. 1. Small polaron hopping in CeO_2. (DFT calculations predict that the reduced Ce-O bond length is 0.091 Å longer than the bond length in a perfect crystal) [2].

Modeling

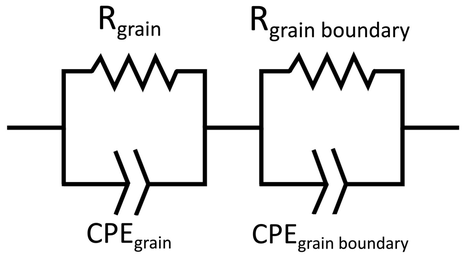

Fig. 2. The EIS equivalent circuit used. Both lattice and grain boundary resistance and capacitance contribute to the AC response. Curve fitting was done in ZView.

Results

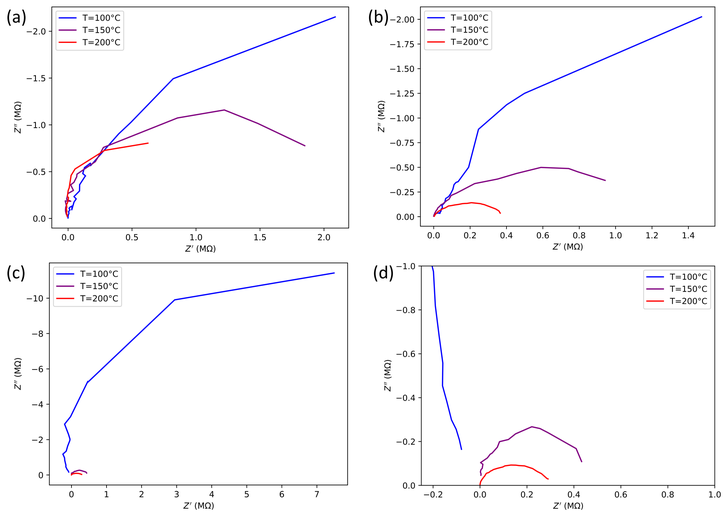

Fig. 3. Nyquist plots for (a), 2% Cu doping, (b), 4% Cu doping, (c), 8% Cu doping. (d) is a magnified version of (c). The AC potential used was 10 mV, and the frequency was swept between 1 MHz and 1Hz.

Table 1. EIS results for each doping concentration at each temperature measured. (When the lattice resistance and grain boundary resistance were similar in magnitude, the model was changed to a single parallel resistor-CPE).

T (°C)	$R_g\ (M\Omega)$	$Q_{0_g}\ (S{\bullet}s^n)$	n_g	$R_{gb}\ (M\Omega)$	$Q_{0_{gb}}\ (S{\bullet}s^n)$	n_{gb}
100°C	3.0712	$2.2279{\bullet}10^{-11}$	1.121	0.26337	$1.7067{\bullet}10^{-10}$	0.92284
150°C	1.9824	$2.469{\bullet}10^{-12}$	1.062	N/A	N/A	N/A
200°C	1.7551	$3.540{\bullet}10^{-12}$	1.033	N/A	N/A	N/A

Nanoparticulate 2% Cu-CeO_2 EIS results for various temperatures

T (°C)	$R_g\ (M\Omega)$	$Q_{0_g}\ (S{\bullet}s^n)$	n_g	$R_{gb}\ (M\Omega)$	$Q_{0_{gb}}\ (S{\bullet}s^n)$	n_{gb}
100°C	24.86	$3.368{\bullet}10^{-13}$	1.055	N/A	N/A	N/A
150°C	0.490280	$2.714{\bullet}10^{-12}$	1.019	$2.008{\bullet}10^{5}$	$5.072{\bullet}10^{-14}$	1.684
200°C	0.207500	$6.6360{\bullet}10^{-10}$	0.8757	0.074913	$9.825{\bullet}10^{-11}$	0.96738

Nanoparticulate 8% Cu-CeO_2 EIS results for various temperatures

T (°C)	$R_g\ (M\Omega)$	$Q_{0_g}\ (S{\bullet}s^n)$	n_g	$R_{gb}\ (M\Omega)$	$Q_{0_{gb}}\ (S{\bullet}s^n)$	n_{gb}
100°C	7.7422	$2.753{\bullet}10^{-10}$	0.84652	0.026272	$2.558{\bullet}10^{-13}$	1.264
150°C	1.017	$1.879{\bullet}10^{-10}$	0.9396	0.142200	$1.807{\bullet}10^{-10}$	0.94181
200°C	0.389860	$8.648{\bullet}10^{-10}$	0.77437	0.000995	$8.092{\bullet}10^{-11}$	1.411

Nanoparticulate 4% Cu-CeO_2 EIS results for various temperatures

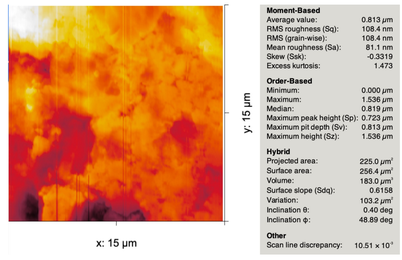

Fig. 4. Sample AFM micrograph of heat-treated pellet surface

Table 2. Relevant pellet dimensions

Composition	Electrode $SA_{top}\ (mm)^2$	Electrode $SA_{bottom}\ (mm)^2$	$SA_{adjusted}\ (mm)^2$	Pellet Thickness (mm)
2% Cu-CeO_2	100	106	115	0.30
4% Cu-CeO_2	95	102	110	0.30
8% Cu-CeO_2	98	103	113	0.30

Conclusions

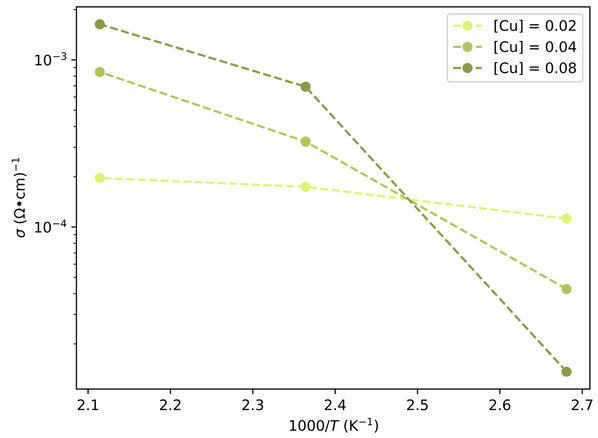

Fig. 5. Arrhenius plot of the three compositions measured.

Table 3. Pre-exponential factor, activation energy, and the mobility, jump rate, and charge carrier density at 200 Celsius for different doping concentrations

Cu (at. %)	$\sigma_0\ (K/(\Omega{\bullet}m))$	$E_a\ (eV)$	$\mu\ (200^\circ C)\ (cm^2/V{\bullet}s)$	$\Gamma\ (200^\circ C)\ (s^{-1})$	$n\ (200^\circ C)\ (m^{-3})$
2%	1.34	0.05	$6.4{\bullet}10^{-2}$	$8.87{\bullet}10^{11}$	$1.90{\bullet}10^{22}$
4%	138	0.21	$1.3{\bullet}10^{-3}$	$1.75{\bullet}10^{10}$	$4.16{\bullet}10^{24}$
8%	4376	0.34	$5.2{\bullet}10^{-5}$	$7.22{\bullet}10^{8}$	$1.96{\bullet}10^{26}$

Future work could involve broadening the range of dopants tested and testing at finer temperature increments. More care could also be taken to shield the impedance bridge, in our case a Solartron 1260A, from vibrations and electromagnetic interference by making use of a Faraday cage, for instance. Polishing the sample surface may also lead to less noise in the low-frequency range of the Nyquist plots.

Synthesis & Preparation

Nanoparticles were synthesized in a 1310-minute co-precipitation reaction. Particles were centrifuged, dried and powderized. Samples were pressed into pellets without binder using 5000 psi of uniaxial pressure for 10 minutes and heat treated up to a maximum temperature of 350°C for 8 hours. Prior PDF analysis done by Haolan Sun showed the particle size ranged from 50 Å to 30 Å depending on the Cu concentration.

Acknowledgements:

Many thanks are due to Professor S.W. Chan and my lab partner Yanhe Li, who have provided me with much guidance and been a joy to work with. Thanks are also due to: Yuan Yang, David Walker, Yves Moussallam, Shuo Ding, Hong Jun Kim, Sam Lossef, Jay Shah, Tianwei Jin, Joe Wild, and Adrian Chitu, without the help of whom this project would not have been possible. *The AFM, optical microscope, and electrode contact paste used in this project were provided by the MSE Teaching Lab.*

References:

[1] H.L. Tuller, A.S. Nowick, Journal of Physics and Chemistry of Solids, Volume 38, Issue 8 (1977) Pages 859-867

[2] José J. Plata, Antonio M. Márquez, and Javier Fdez. Sanz, The Journal of Physical Chemistry C (2013) 117(28)