

A novel efficient oxide electrode for electrocatalytic oxygen reduction at 400-600 °C

Wei Zhou, Zongping Shao*, Ran Ran, Wanqin Jin, Nanping Xu

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, No.5 Xin Mofan Road, Nanjing, 210009, P.R. China.

E-mail: shaozp@njut.edu.cn; Fax: 86-25-83365813; Tel: 86-25-83587722

Experimental Section

Powder Synthesis and cell fabrication

$\text{SrNb}_{0.1}\text{Co}_{0.9}\text{O}_{3-\delta}$ (SNC) was synthesized by a solid-phase reaction with SrCO_3 , Nb_2O_5 and Co_2O_3 (all in analytical grades) applied as the raw materials for the metal sources. The raw materials were weighed and well mixed using a FRITSCH Pullerisette 6 high-energy ball miller under acetone liquid media at the rotation of 500 rpm for 30 min. After drying, the primary powders were calcinated at 1100~1200 °C in air for 10~20 h to form the oxides with the final lattice structure. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) was synthesized by a combined EDTA-citrate complexing sol-gel process. Metal nitrates $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, and $\text{Fe}(\text{NO}_3)_3$ were used as the raw materials. Each metal nitrate was prepared as a separate aqueous solution, and a standard EDTA titration method was used to determine the precise concentrations of these solutions. The required amounts of metal nitrate solutions were mixed, and EDTA and citric acid were added to serve as complexing agents. The pH value of the solution was adjusted to ~6 with NH_4OH . The molar ratio of total metal ions/EDTA/citric acid was set at 1:1:2. The water was evaporated at 90 °C yielding transparent gels. The gels were pre-fired at 250 °C and then calcinated at 1000 °C for 5 hours under an air atmosphere, and the resulting products possessed the desired final phase structure.

Symmetrical cells with electrode|SDC|electrode configurations were fabricated for the impedance studies. Dense SDC pellets, which were 12.0 mm in diameter and 0.8 mm thick, were prepared through dry pressing. The pellets were then sintered at 1350 °C for 5 hours. The SNC or BSCF cathode powder was first dispersed in a pre-mixed solution of glycerol, ethylene glycol, and isopropyl alcohol, and a colloidal suspension was formed via high-energy ball milling (Fritsch, Pulverisette 6) at 400 rpm for 0.5 hours. The resulting slurry was painted onto both surfaces of the SDC pellet in symmetric fashion and subsequently calcined at 1000 °C for 2 hours under an air atmosphere.

The performance of the cathode was also evaluated in a complete electrochemical cell. Anode-supported thin-film electrolyte dual-layer cells were prepared via dual dry-pressing and subsequent high-temperature sintering. Anode powders consisting of NiO and SDC (Ni: SDC=50: 50 vol%) were prepared through the mechanical mixing of NiO and SDC in an agate mortar. The electrolyte of the green bi-layer pellets was

densified through firing at 1450 °C for 5 hours under an air atmosphere. The cathode slurry was then painted onto the central surface of the densified electrolyte and fired at 1000 °C for 2 hours under an air atmosphere. The resulting coin-shaped cathode was 20 µm thick and had an effective area of 0.48 cm².

A three-electrode system was used to get the cathodic overpotential-current density curves. The SSC slurry was painted on one side of the SDC electrolyte to form an electrode area of 0.26 cm², used as working electrode (WE). Silver paste was painted on the other side of the SDC pellet in symmetric configuration, as the counter electrode (CE) and the reference electrode was painted as a ring.

Electrochemical characterization

The *I*-*V* polarization was measured using a Keithley 2420 source meter. H₂ fuel was fed into the anode chamber at a flow rate of 80 ml min⁻¹ (STP), and ambient air served as the oxidant gas. The electrochemical impedance spectra of the cathode were investigated via an ac impedance method using an electrochemical workstation composed of a Solartron 1260A frequency response analyzer and a Solartron 1287 potentiostat. The applied frequency range was from 0.01Hz to 100 kHz, and the signal amplitude was 10mV under open cell voltage (OCV) conditions. Cathodic overpotential was measured using a Solartron 1287 potentiostat/galvanostat.

Other characterization

Electrical conductivity was measured by the four-terminal DC technique in air, using Ag paste as electrodes. The current and the voltage were detected by Keithley 2420 source meter at intervals of 10 °C within a temperature range of 350-725°C. The oxygen nonstoichiometry at high temperatures was measured by thermogravimetry (TG) analyses (Model STA 409, NETZSCH) carried out in flowing air. Oxygen nonstoichiometry of the samples at room temperature was evaluated by iodometry method. Briefly, the samples with the weight of 0.1000 g were dissolved in HCl (6.0 mol l⁻¹) under an inert gas atmosphere in order to prevent the oxidation of I⁻ ions by air, and then the solution was titrated by standard thiosulfate solution. Morphologies of the cathodes were observed using scanning electron microscopy (SEM, Hitachi, S3400).

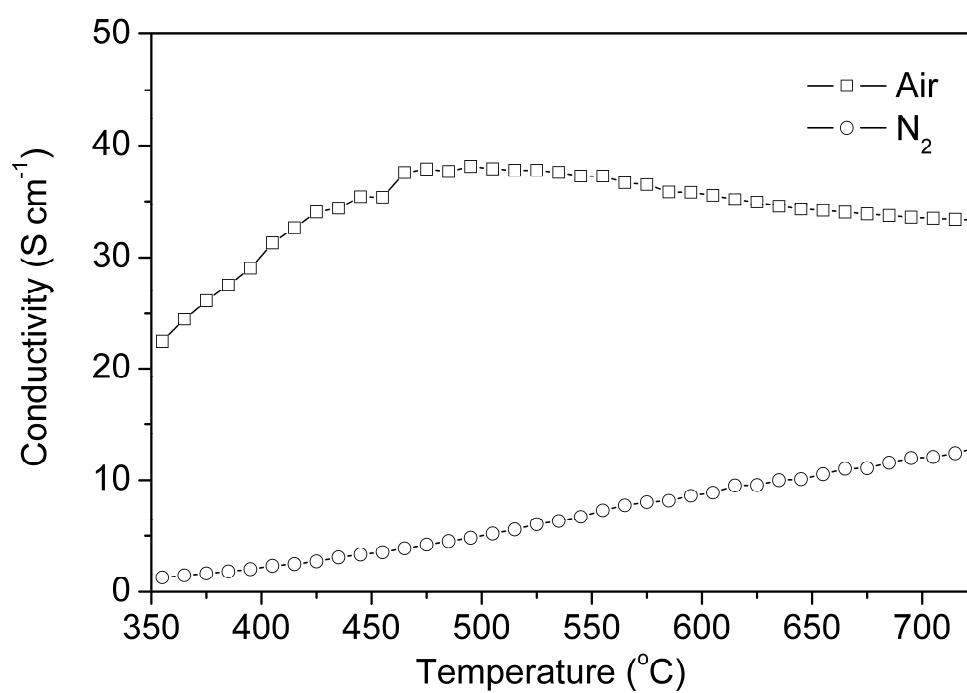


Figure S1 Temperature dependence of electrical conductivity of BSCF measured in air and N₂.

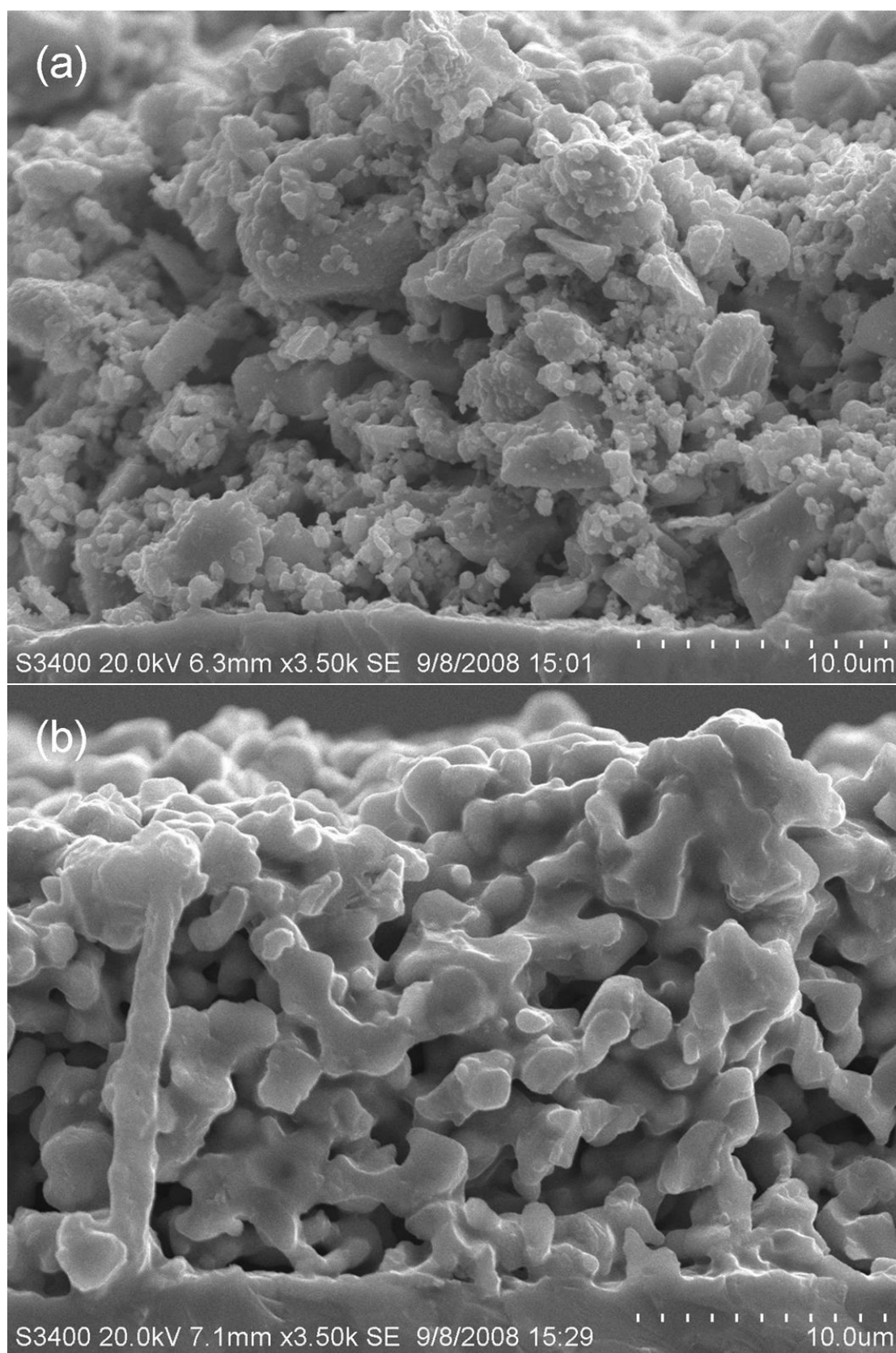


Figure S2 SEM micrographs of the cross section of the SNC (a) and BSCF (b) cathodes.

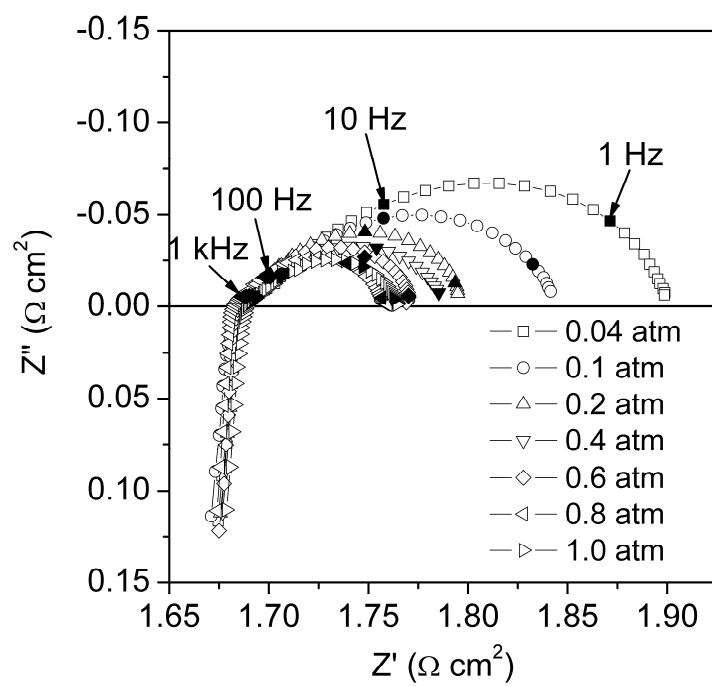


Figure S3 Nyquist plots of the cells with the SNC cathode at 600 °C under various $P(\text{O}_2)$.

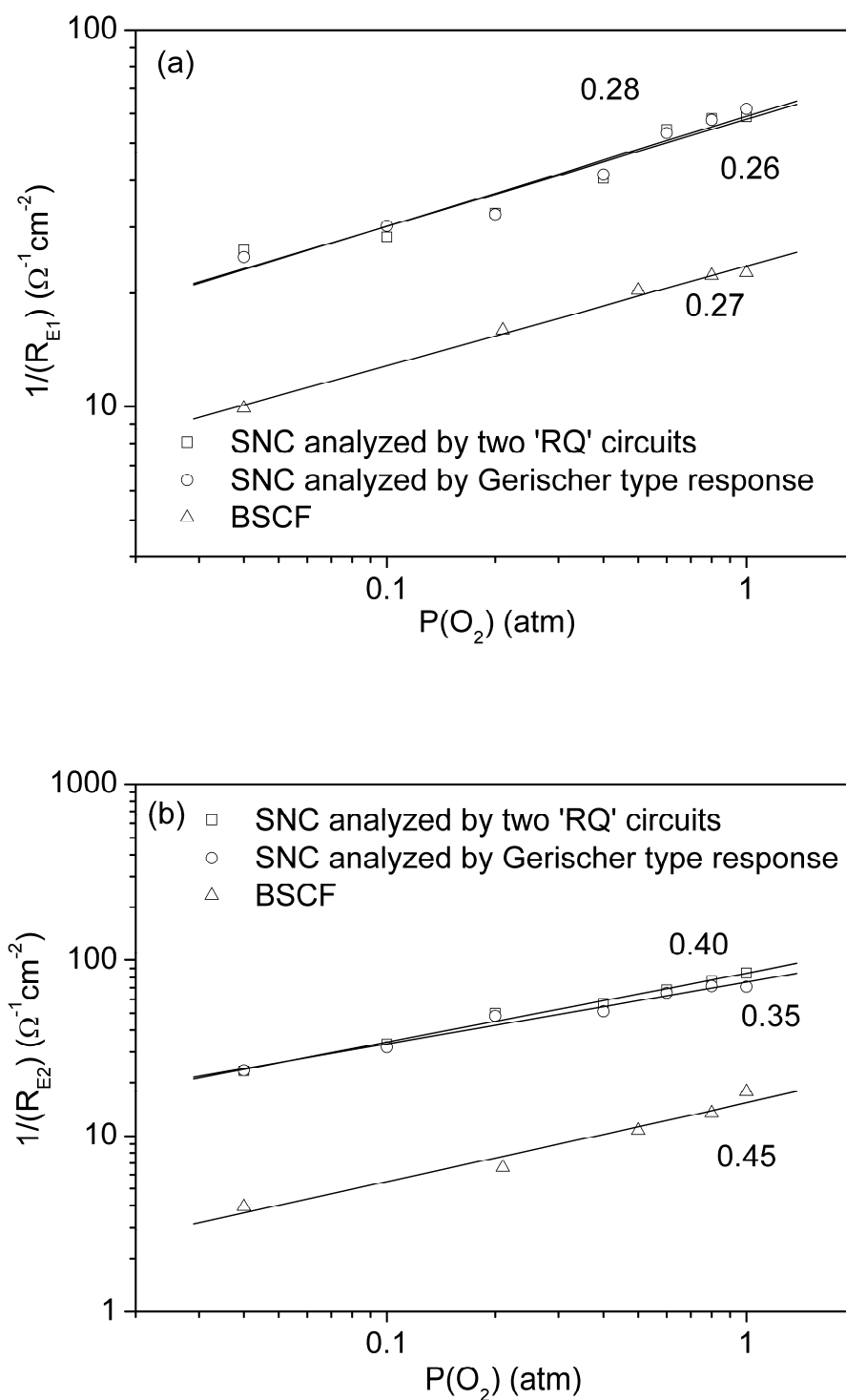


Figure S4 PO_2 dependence of R_{E1} and R_{E2} measured at 600 °C. We have also used a 'Gerischer' type response to analyze the impedance.¹ As a result very similar results are obtained from the both methods.

1 S.B. Adler, J.A. Lane and B.C.H. Steele, *J. Electrochem. Soc.*, 1996, **143**,3554.

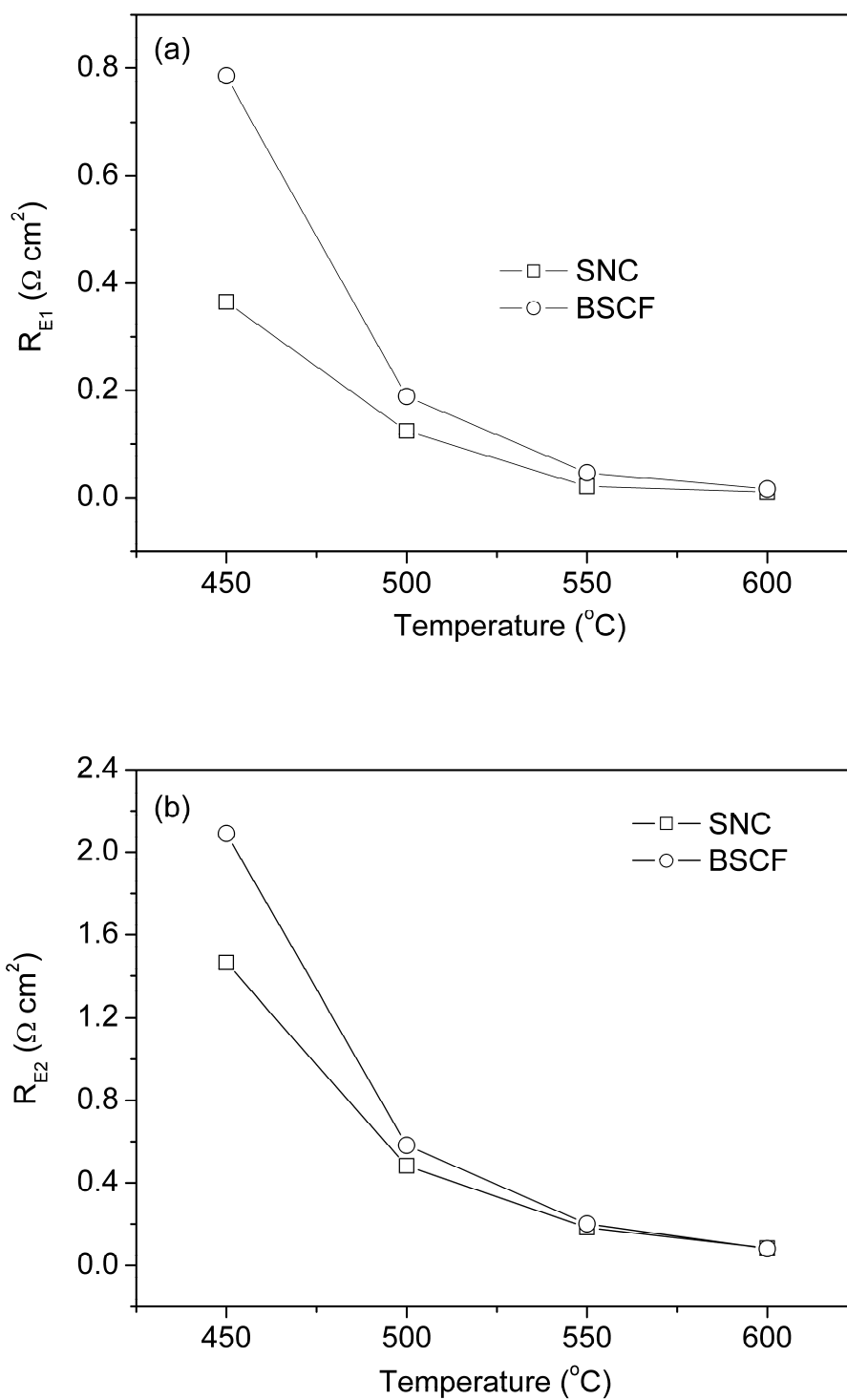


Figure S5 Temperature dependence of R_{E1} and R_{E2} measured in air.