

Supplementary Information

A new energy conversion technology joining electrochemical and physical principles

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1. Experimental

1.1 Materials preparation

The electronic/semi- conducting materials in the single-component device were prepared for LiNiCuZn based oxides by solid state reaction methods. Stoichiometric amounts of Li_2CO_3 , $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, USA) were mixed grounded and sintered at 800 °C for 2-4 hours. Some typical compositions with a molar ratio among metal elements are: Li:Ni:Cu:Zn = 3:6:3:6. The material obtained was again mixed with an ionic conductor, $\text{Ce}_{0.8}\text{Sm}_{0.2-x}\text{O}_{2-\delta} \cdot \text{Na}_2\text{CO}_3$ (NaSDC) nanocomposite¹⁰ with 2: 1 to 1: 2 weight ratios. The mixed powder was further heated at 700 °C for 1 hour then pressed uniaxially with a 100-300 MPa load to flat tablets of the single-component material, on which both end surfaces were pasted by silver as current collectors. The tablet diameter was normally 1.3 cm and its thickness 0.06 – 0.10 cm. The larger area units of $6 \times 6 \text{ cm}^2$ were constructed for the single-component device by

hot-pressing technique at 600 °C and a pressure of 10–20 tons. Silver coated metal nets were used on both sides as current collectors for the large area cell.

1.2 Fuel cell measurements

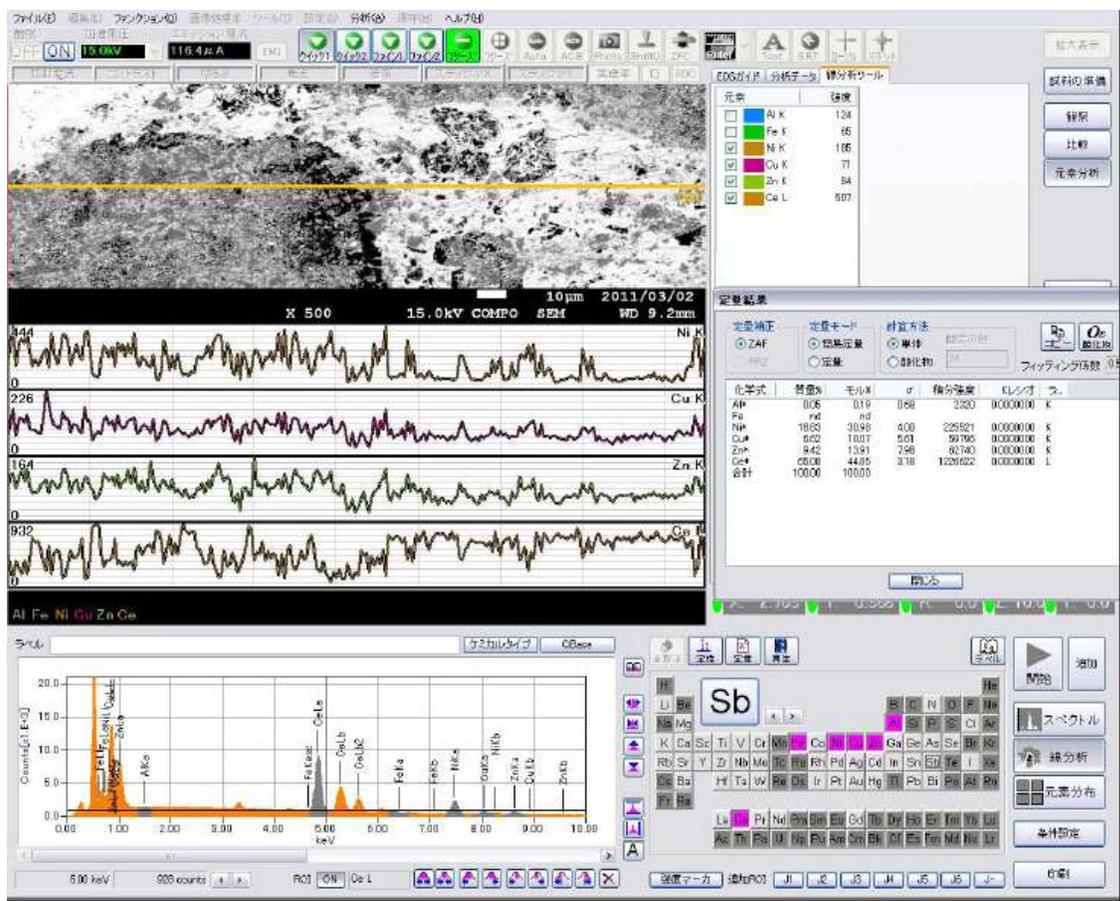
The fuel cells were measured using a computerized instrument (Sm-102, Inc, Tianjin, China) over the temperature range of 400 – 600 °C. Hydrogen and air were supplied in the range of 80 – 110 ml min⁻¹ under 1 atm on each side for 1.3 cm cell, and 1–2 × 10³ ml min⁻¹ for 6 × 6 cm² cell. Hydrocarbon fuels were also tested. Biogas containing 20% H₂, 54% CO, 12% CO₂, and 14% CH₄ was supplied at 75 ml min⁻¹ and the air at 100-120 ml min⁻¹; the methanol and ethanol were mixed by water in a volume ratio 50:50 and fed to the testing single component device at 3 ml min⁻¹ and the air at 100-120 ml min⁻¹. A detailed device and setup is further illustrated in Figure S5.

1.3 Electrochemical analysis

EIS spectra were performed using a VERASTA2273 (Princeton Applied Research, Oak Ridge, TN, U.S.) analyzer under the open circuit voltage from 0.01 Hz to 1M Hz with the amplitude of 10 mV at various temperatures both in air and H₂ for 1.3 cm pellet.

2. Materials characterizations and properties as well as device performances

Supplementary Figure S1: The picture is backscattered electron image obtained from SEM analysis, and the contrast represents different compositions, from which we can see the homogeneous distribution. Selected four typical elements' line scanning/mapping results further prove homogeneous distribution of the component compositions.



Supplementary Figure S2:

Single component device results for various fraction of ceria (0, 30, 60, 70 wt%, respectively) to the LiNiCuZn oxides at 550 °C, respectively; (a), (b), (c) and (d) contain ionic conducting phase, SDC, 0, 30, 60, 70 wt%, respectively.

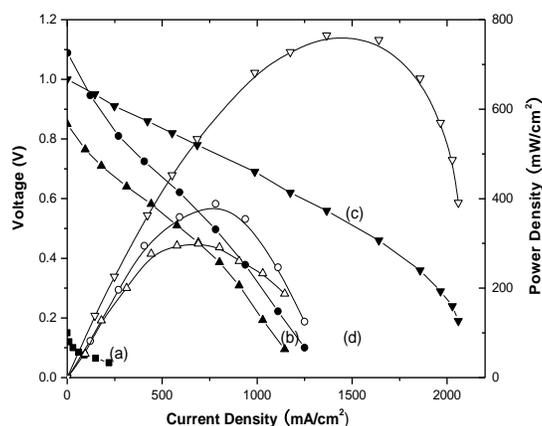
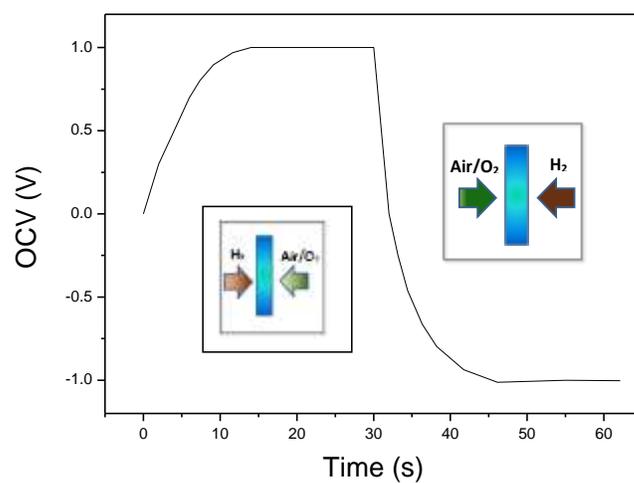


Figure S2 shows single component device performances with various compositions of the LiCuNiZn- SDC. It can be seen that device OCVs strongly depend on the ratios between the electronic and ionic phases from almost short circuit case, 0.15 V, Fig. S2a, corresponding to major electronic conduction causing a short circuiting behavior; while increasing the ionic phase above 30 wt% (30SDC-70LiNiCuZn), the OCV increases significantly up to 0.85 V as well as power output up to about 300 mW/cm², see Fig. S2b; Continued to increase the ionic phase to 60wt% (60SDC-40LiNiCuZn), both device voltage and power output are increased greatly to 1.0 V and 760 mW/cm² reached as shown in Fig. S2c. Though further increasing the ionic phase the OCV is slightly increased up to 1.1 V, the device performances decrease, Fig. S2d. In this case, an ionic conducting dominates the material conducting behavior due to low electronic phase used. It has been observed that the well balanced electronic and ionic phases and conductivities are very important to achieve the best device performances.

These results may be compared with conventional SOFCs that in order to deliver effective power, both electronic and ion conductivities have to be used in electrodes. The SOFC anode and cathode always use the mixture of anode or cathode with the electrolyte (ion conductor) to prepare so called composite electrodes.

Supplementary Figure S3: A single component device OCV response during switching H₂ and air supplies



Supplementary Figure S4:

The durability test for more than 50 hours for the device discharged under a constant Load.

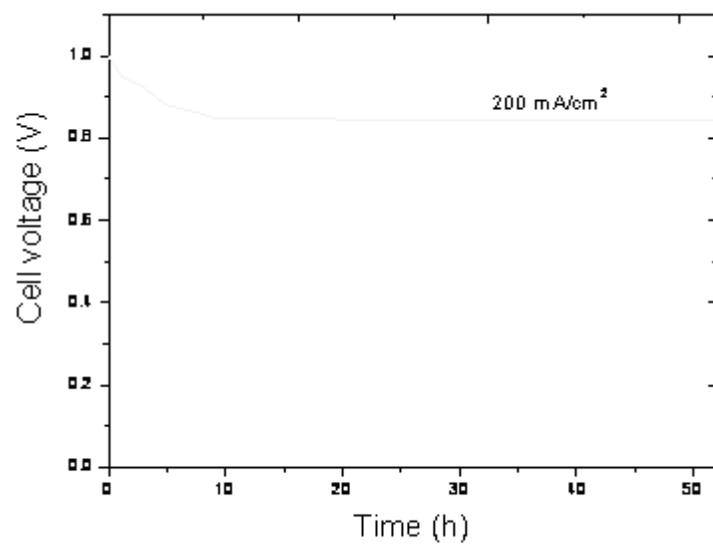


Figure S5 testing device and setup

