Supplementary material

Modified DC Hebb-Wagner polarization method for determining the partial protonic electrical conductivity in mixed-conducting $BaGd_{0.3}La_{0.7}Co_2O_{6-\delta}$

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In the proposed modified DC-4 wire Hebb-Wagner technique, the microstructure of the platinum internal Pt(2) electrode is important. It must be porous to ensure a mixed transport of gaseous H_2 and protonic defects continuously throughout the HW cell. In this work, we used a platinum paste (ESL 5542, Electroscience Inc.) which was heated in a static air atmosphere at 930 °C for 0.5 h. The SEM images of the porous Pt layer used in this work are shown in Figure S1. As can be seen, the platinum Pt(2) electrode is porous, with an average grain size of less than 1 µm.

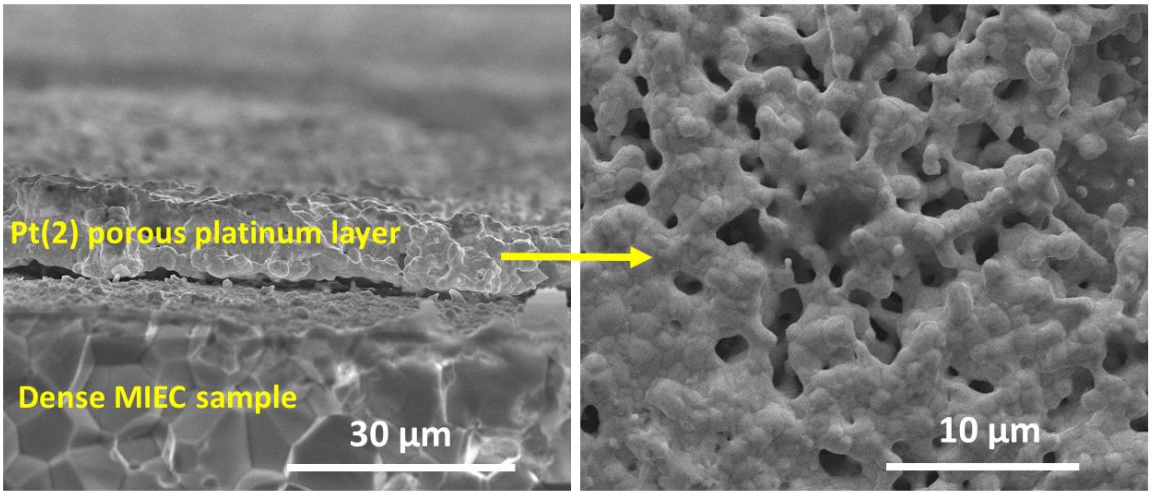

Figure S1. *SEM images of MIEC/Pt(2) interface and surface of the porous platinum electrode.*

A layer of dense gold (ESL 8880, Electroscience Inc.) was applied to the side surface of the system to block the molecular transport of oxygen and water vapor to the MIEC and LCNO samples. Dense gold has a negligible transference number for oxygen ions and protons and is

a pure electronic conductor. Also, the transport of neutral oxygen species across grain boundaries, which can sometimes happen in dense platinum, does not occur in gold (Ilan Riess, 2014, private communication). Figure S2 shows an SEM photo of the gold layer used in the studied HW cell. As can be seen, the layer is completely dense, with no visible pores. Therefore, the transport of gaseous oxygen and H_2O to the material did not occur during the measurement.

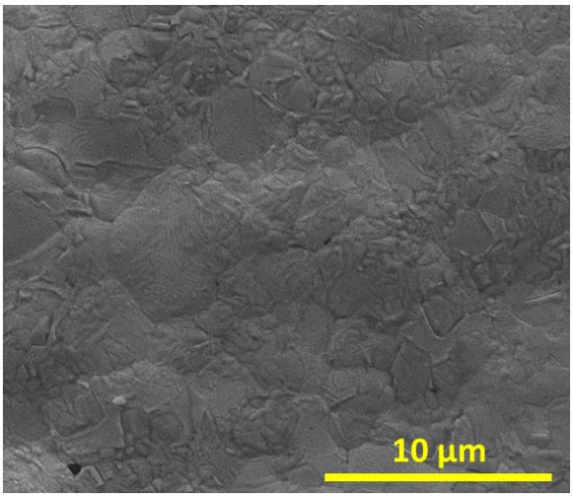

Figure S2. *SEM image of dense gold layer used for sealing of HW-cell.*

Figure S3 shows the typical system we use for electrical measurements, e.g. HW technique. We use a self-made cell, which is mounted to a home-built tube furnace (all marked in Fig.S3).

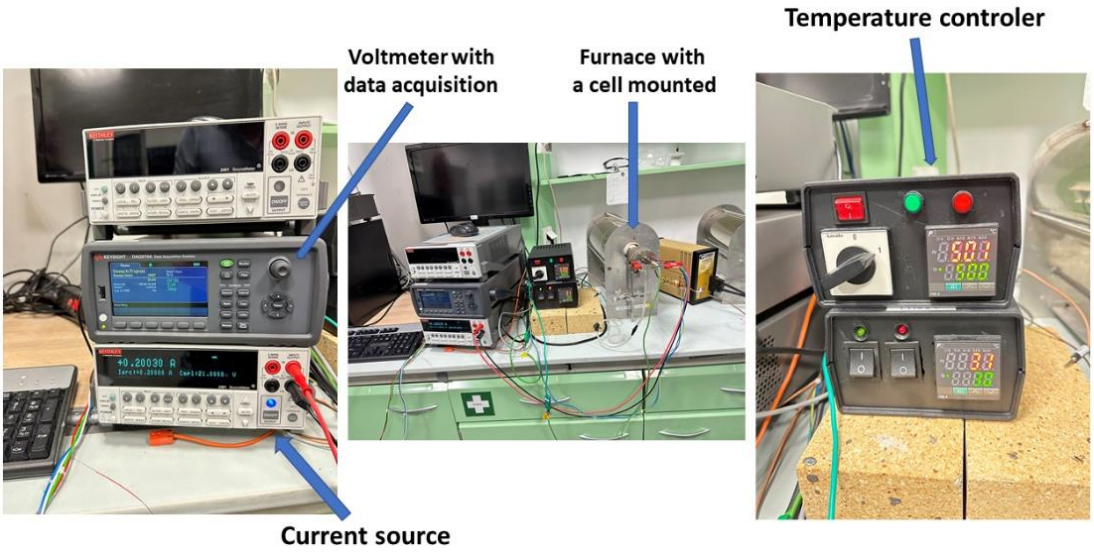

Figure S3. *The images of the electrical measuring apparatus and the furnace with mounted measurement cell.*

The furnace is controlled by a temperature controller with a built-in PID controller. The thermocouple controlling the furnace is type K. The current source e.g. Keysight 2401 and a voltmeter with data acquisition e.g. Keysight 34970A or DAQ970A are connected to the measuring chamber (marked in Fig.S3). The constant current was set on the current source with high accuracy, and voltage measurements were monitored by PC on *BenchLink Data Logger Pro Software* with a 2 s time interval between each measurement.