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Gel-combustion synthesis of $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ and measurement of its humidity-dependent electrical conductivity

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Mixed ionic and electronic conducting (MIEC) oxides have potential applications as sensors, as oxygen separation membranes, in membrane reactors for *syn gas* production, and as cathodes for solid oxide fuel cells [1]. $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ or LSCF is a well-known MIEC oxide which enjoys a greater degree of mechanical and chemical stability than other mixed conducting oxides, and hence has been studied extensively. Substituting Sr and Co on the La and Fe sites decreases the high-temperature phase stability of $LaFeO_3$ and the material becomes highly oxygen deficient at elevated temperatures and reduced oxygen partial pressures [2]. Our earlier studies on acceptor doped perovskites revealed that these oxygen deficient perovskites can be candidate materials for moisture detection with a wide range of linearity and narrow hysteresis loop [3]. Hence the present study was undertaken to study the humidity-dependent DC conductivity on the well-known oxygen deficient mixed conductor $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$.

LSCF was prepared by gel-combustion method employing reagent grade $La(NO_3)_3{\cdot}6H_2O$, $Sr(NO_3)_2$, $Fe(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, and glycine. The glycine-to-nitrate ratio is 2:1. The glycine-nitrate process is a self-sustaining gel-combustion synthesis technique that produces fine, homogeneous metal-oxide powders. Aqueous precursor solutions containing metal nitrate and glycine are heated on a hot plate in a vented cabinet until they auto-ignite, producing metal-oxide "ash." Glycine serves a dual role: in the precursor solution, glycine complexes the metal cations, thereby preventing selective precipitation and upon ignition, glycine is oxidized by the nitrate ions, thereby serving as the fuel for the combustion reaction [4].

The phase purity of the synthesized powder was confirmed by powder X-ray diffraction (XRD) technique. Microstructural studies were carried out in a scanning electron microscope (Jeol JSM 5600 LV). The synthesized powders were pulverized, compacted into cylindrical pellets, and sintered at 1250 °C for 6 hr in air. The density of the pellets was measured by Archimedes' principle. For electrical conductivity measurements, two electrodes of fine copper wire (0.14 cm diameter) were connected onto the sample by electrode grade silver paint (GE Thorsen). The sample was connected to a DC power supply and a picoammeter (Keithley 485) in series. The sensor signal was obtained by applying a small voltage between the electrodes and the corresponding current in the circuit was measured at constant temperature. The generation of the required relative humidity ambience and the evaluation of response and recovery characteristics were carried out using the procedure reported elsewhere [5].

The XRD of $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ is given in Fig. 1. The XRD patterns confirmed the formation of the perovskite with the expected rhombohedral phase symmetry [6]. The average crystalline size was calculated from the X-ray pattern using the Scherrer equation and is in the range 10–35 Å. The SEM of the LSCF sintered at 1250 °C is given in Fig. 2, which shows that the sample is of relative density greater than 95%. It can be identified from the SEM that the average grain size is between 1 and 3 μm.

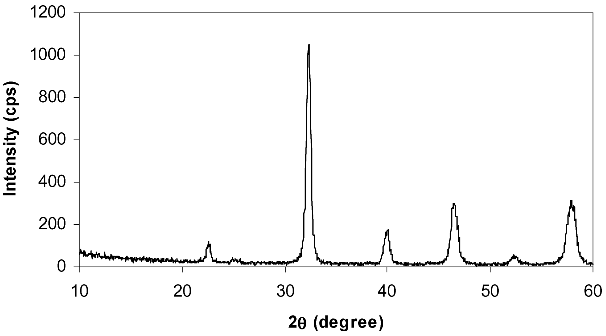

Figure 1 The powder XRD pattern of $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$.

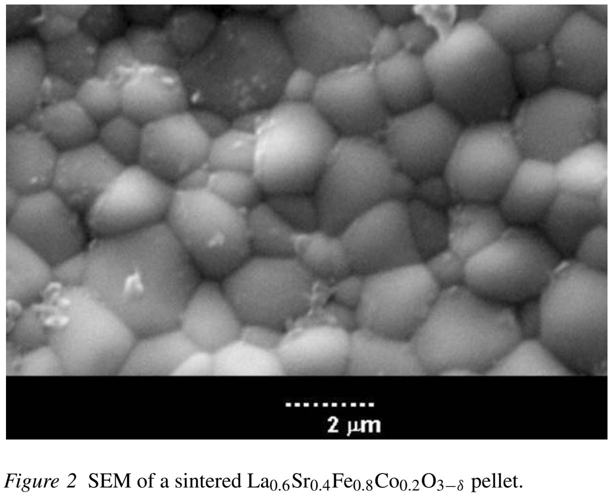

Figure 2 SEM of a sintered $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ pellet.

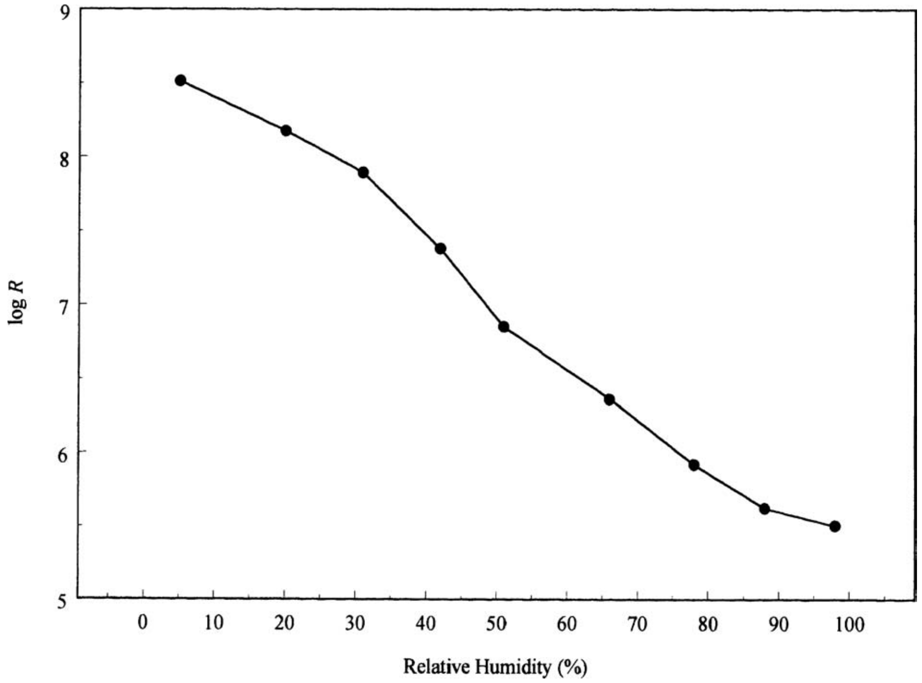

Figure 3 Relative humidity vs. log R plot at room temperature for $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$.

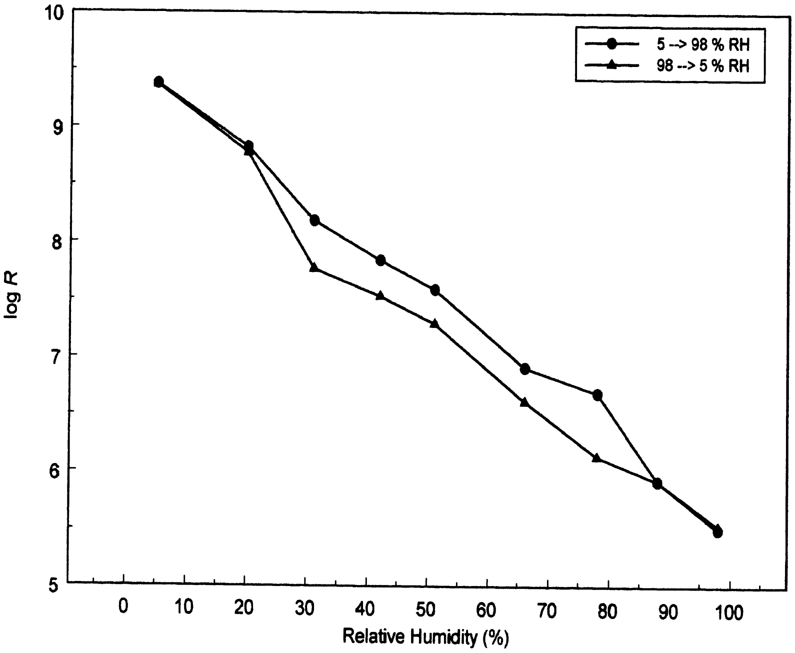

Figure 4 Adsorption and desorption behavior of $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ at 25 °C.

The ohmic nature of the electrode contacts was ascertained from the linear dependence of the measured current with applied field at constant temperature. The sample was statically housed under each RH with equal time intervals until equilibrium was reached. The results of resistance measurements as a function of relative humidity at a fixed ambient temperature of 27 °C are presented in Fig. 3. The DC resistance of LSCF was in the range of 10^8 Ω in dry air, and it drops by almost three orders of magnitude when the relative humidity is increased from 5 to 98% RH. The significant feature is that the variation in log R with RH (%) is almost linear in the entire range of study, which is a prerequisite for commercial humidity sensors. The sensitivity factor (S_f), which is $R_{5\%}/R_{98\%}$, where $R_{5\%}$ and $R_{98\%}$ are the DC resistances at 5 and 98% RH, respectively, is calculated to be 7420. Adsorption and desorption behavior of LSCF in humid atmosphere was studied at 27 °C and is presented in Fig. 4. The resistance of the sample was continuously measured at equal intervals between 5 and 98% RH. LSCF exhibited remarkably narrow hysteresis indicating facile adsorption and desorption of water.

The DC resistance, measured alternatively in dry and wet air, helped establish the response and recovery characteristics as shown in Fig. 5. The invariant resistance in dry air is in the order of 10^8 Ω. Within about 200 s of purging with moist air, the resistance drops by three orders of magnitude to reach a constant value. The time taken for the restoration of the original signal is 350 s and the sample becomes very sensitive to further changes in humidity. This further indicates that water

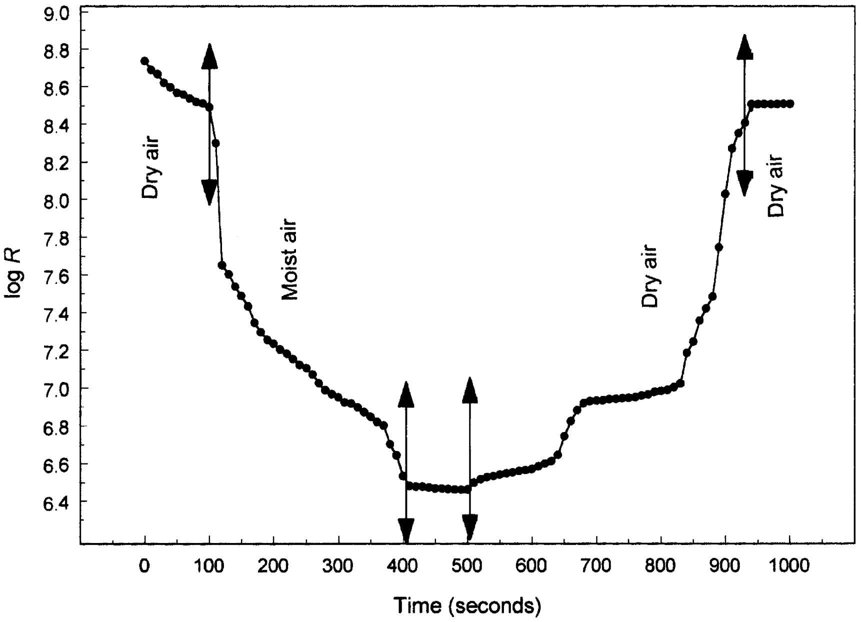

Figure 5 Log *R* vs. time plot of $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ exposed to dry and moist air alternatively at room temperature.

molecules can be adsorbed or desorbed reversibly at room temperature on the LSCF surface.

To conclude, this paper reports the gel-combustion synthesis of LSCF which exhibits remarkably good sensitivity to moisture, linearity in the entire RH range, and narrow hysteresis. The influence of oxygen vacancies on the moisture sensitivity remains unclear and is currently under investigation.

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