SUPPORTING INFORMATION

Bismuth Doped Lanthanum Ferrite Perovskites as Novel Cathodes for Intermediate-temperature Solid Oxide Fuel Cells

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The ECR method is developed for a single phase mixed conductor such as $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ whose conductivity (σ) and oxygen nonstoichiometry (δ) depend on oxygen partial pressure, Po_2. Its theoretical approach is briefly summarized below. In the measurement, variation in conductivity is resulted from the step change of Po_2. A linear relation is assumed between the changes of the electrical conductivity and the concentration of the lattice oxygen/the oxygen vacancy.[1] The conductivity is normalized according Eq. (1a) and is fitted to a solution of Fick's second law (Eqs. (1b, 1c, 1d)).[2,3] The variable parameters in data fitting are the chemical surface exchange coefficient, K_{chem} (cm s^{-1}), and the chemical bulk diffusion coefficient, D_{chem} (cm^2 s^{-1}). In the following equations, K_{chem} and D_{chem} are represented by k and D for simplify.

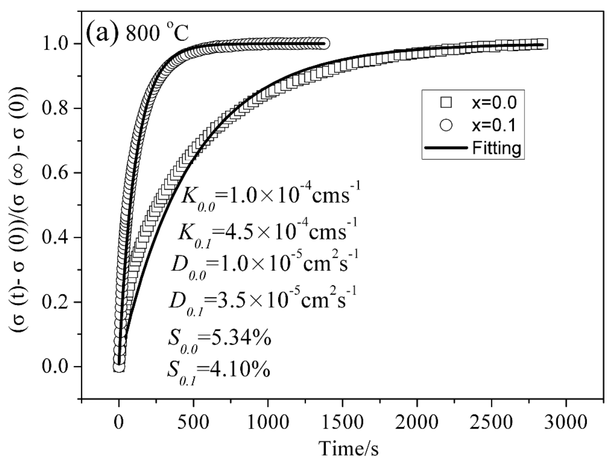
$$n(t)=\frac{\sigma(t)-\sigma(0)}{\sigma(\infty)-\sigma(0)}=\frac{c(t)-c(0)}{c(\infty)-c(0)}=\frac{M(t)}{M(\infty)} \tag{1a}$$

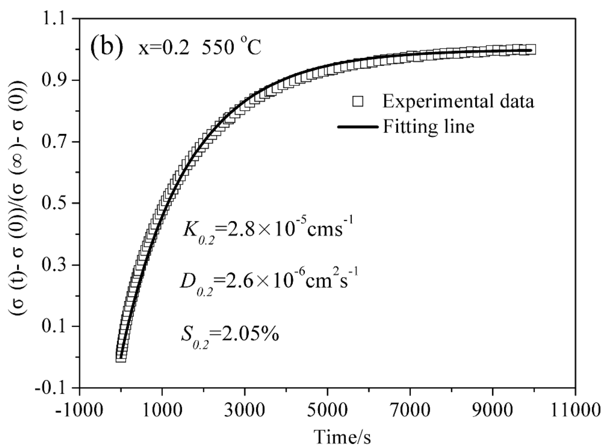
$$\frac{M(t)}{M(\infty)}=1-\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\sum_{p=1}^{\infty}\frac{2L_\beta^{\ 2}\exp(-\beta_n^{\ 2}Dt/x^2)}{\beta_m^{\ 2}(\beta_m^{\ 2}+L_\beta^{\ 2}+L_\beta)} \times\frac{2L_\gamma^{\ 2}\exp(-\gamma_n^{\ 2}Dt/y^2)}{\gamma_n^{\ 2}(\gamma_n^{\ 2}+L_\gamma^{\ 2}+L_\gamma)}\times\frac{2L_\phi^{\ 2}\exp(-\phi_p^{\ 2}Dt/z^2)}{\phi_p^{\ 2}(\phi_p^{\ 2}+L_\phi^{\ 2}+L_\phi)} \tag{1b}$$

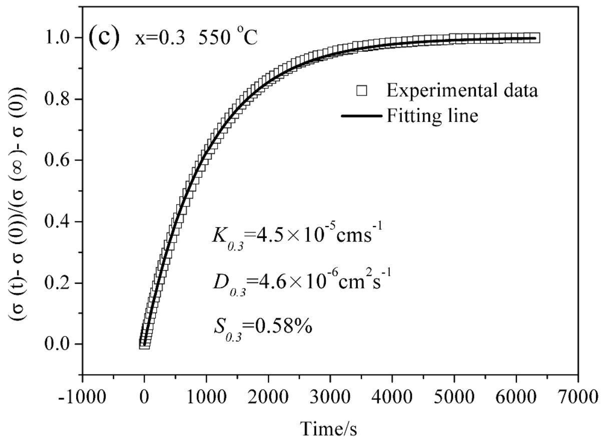
$$\beta_m\tan\beta_m=L_\beta;\ \gamma_n\tan\gamma_n=L_\gamma;\ \phi_p\tan\phi_p=L_\phi \tag{1c}$$

$$L_\beta=\frac{x}{L_c};\ L_\gamma=\frac{y}{L_c};\ L_\phi=\frac{z}{L_c};\ L_c=\frac{D}{k} \tag{1d}$$

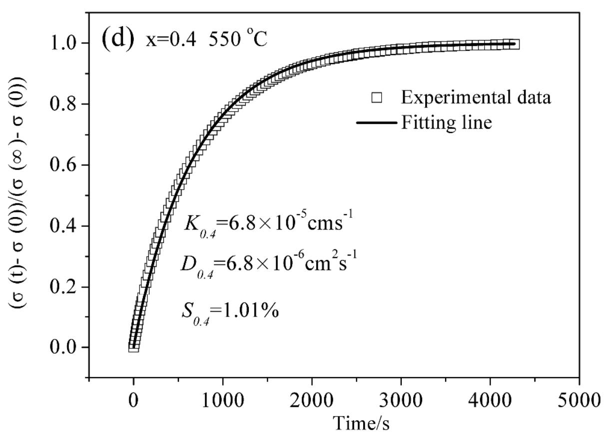
where t is time in seconds; $n(t)$ is normalized conductivity; $\sigma(t)$ is instantaneous conductivity at time t, $\sigma(0)$ initial conductivity at equilibrium for the original Po_2, and $\sigma(\infty)$ is conductivity at equilibrium for the step changed Po_2; $c(t)$ is the oxygen ion concentration at time t, $c(0)$ initial oxygen ion concentration at equilibrium for the original Po_2, and $c(\infty)$ the oxygen ion concentration at the equilibrium to the step changed Po_2; $M(t)$ is the amount of oxygen entering or leaving the single phase sample at time t; $M(\infty)$ is the total amount accumulated when the diffusion proceeds for an infinite time, the time to reach the equilibrium; x, y and z are dimensions of the sample in centimeters. The smallest dimension, z, is often referred as the sample thickness, $L=z$. L_c is the critical thickness; and β_m, γ_n, ϕ_p are the positive, non-zero roots of Eq. (1d). By fitting the experimental data with Fick's second law, K_{chem} and D_{chem} could be obtained. Figure S1 shows the typical experimental data and the fitting results for $La_{0.8-x}Bi_xSr_{0.2}FeO_{3-\delta}$ ($0 \le x \le 0.8$).



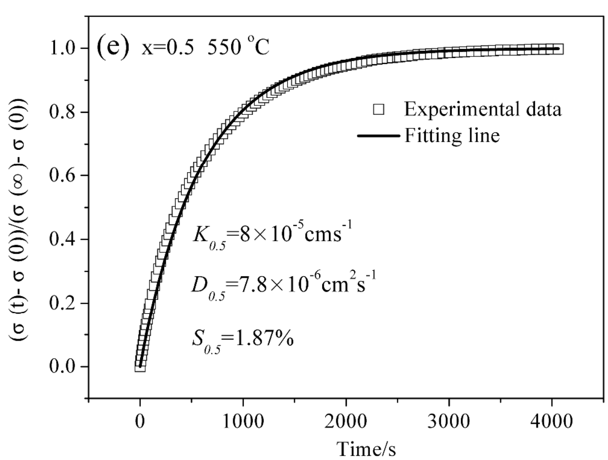




(c) x=0.3 550 °C
Experimental data
Fitting line
$K_{0.3}$=4.5×10^{-5}cms^{-1}
$D_{0.3}$=4.6×10^{-6}cm^{2}s^{-1}
$S_{0.3}$=0.58%
(σ (t)- σ (0))/(σ (∞)- σ (0))
Time/s



(d) x=0.4 550 °C
Experimental data
Fitting line
$K_{0.4}$=6.8×10^{-5}cms^{-1}
$D_{0.4}$=6.8×10^{-6}cm^{2}s^{-1}
$S_{0.4}$=1.01%
(σ (t)- σ (0))/(σ (∞)- σ (0))
Time/s



(e) x=0.5 550 °C
Experimental data
Fitting line
$K_{0.5}$=8×10^{-5}cms^{-1}
$D_{0.5}$=7.8×10^{-6}cm^{2}s^{-1}
$S_{0.5}$=1.87%
(σ (t)- σ (0))/(σ (∞)- σ (0))
Time/s

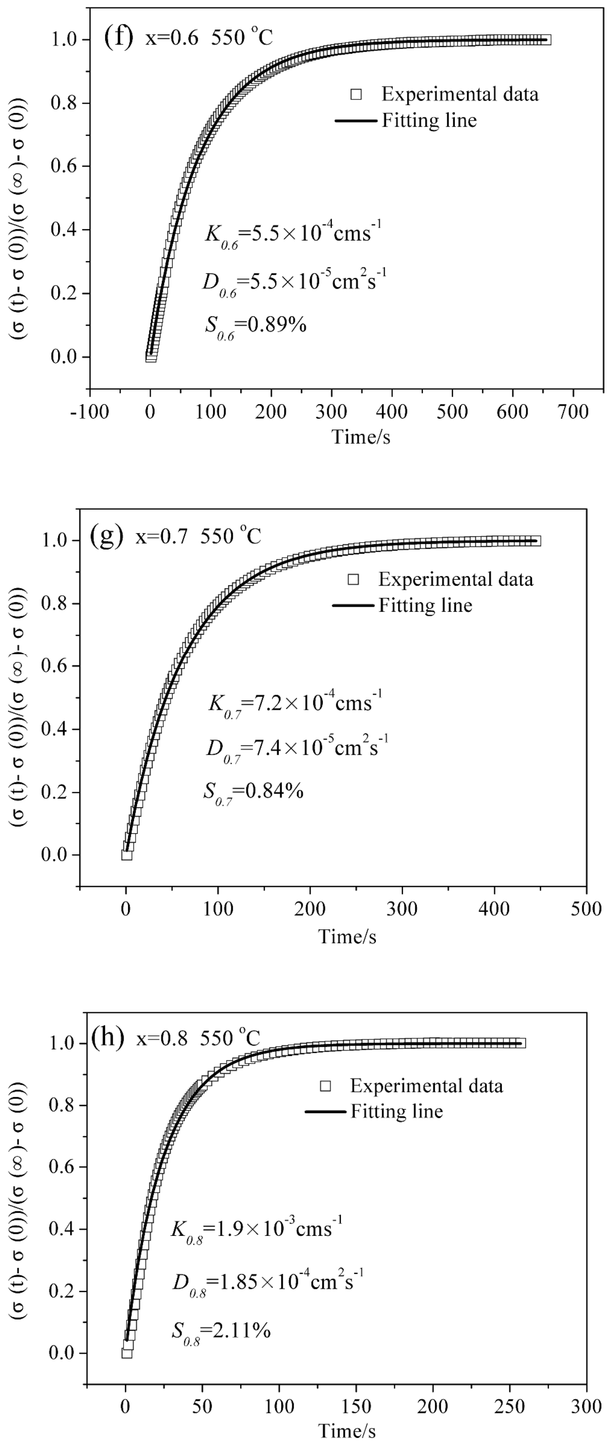


Figure S1. Experimental data and fitting curves of conductivity change profiles as a function of relaxation time for $La_{0.8-x}Bi_xSr_{0.2}FeO_{3-\delta}$ ($0 \leq x \leq 0.8$). (a) x = 0 and 0.1 at 800 ^oC. (b) x=0.2, (c) x =0.3, (d) x =0.4, (e) x =0.5, (f) x =0.6, (g) x =0.7, and (h) x

=0.8 at 550 ^{o}C.

REFERENCES

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