

# Supporting Information

## Substrate and Thickness Effects on the Oxygen Surface Exchange of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ Thin Films

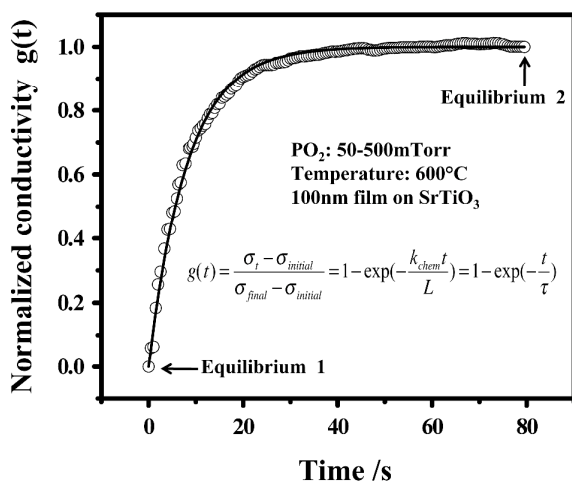
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**KEYWORDS:** Surface exchange, thin films, strain, dislocations, solid oxide fuel cells,  $(\text{La},\text{Sr})\text{MnO}_3$

### Transient normalized conductivity

A typical time-dependent change in the normalized conductivity is shown in Figure S2. This data is for the 100 nm thick film on  $\text{SrTiO}_3(100)$ , measured at 600 °C during a change in  $p\text{O}_2$  from 50 to 500 mTorr. A similar curve for the same film at 700 °C was given elsewhere.<sup>1</sup> The film conductivity varied with time in an exponential fashion until the new equilibrium was established (in this case for the oxidation process). The solid line given in the curve is the fit using the Eq. 1 (shown in the figure). All curves exhibited similar qualities of fit.

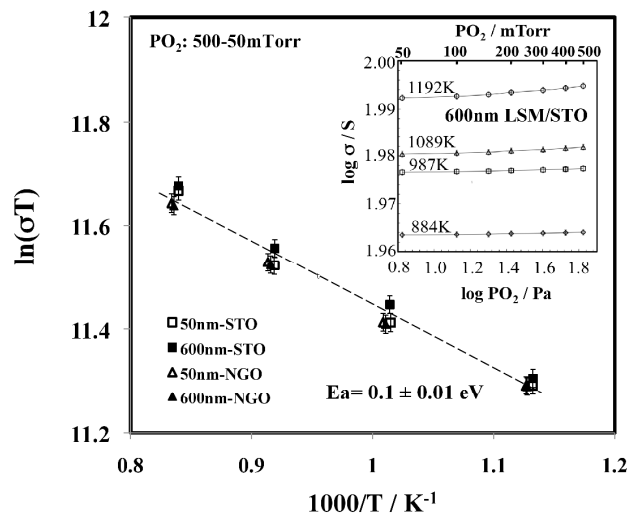


**Figure S1.** Surface exchange coefficients of 100 nm films on STO (100) and NGO (110) as a function of film thickness during both oxidation and reduction processes.

### Steady state conductivity

In order to confirm the steady state conductivity of the films were representative of typical LSM materials,  $\sigma(T, p\text{O}_2)$ , were measured as a function of temperature ( $600 \leq T \leq 900$  °C) and oxygen pressure ( $50 \leq p\text{O}_2 \leq 500$  mTorr) for all films. Thickness and substrate have little effect on  $\sigma(T, p\text{O}_2)$ , as seen in Figure S1, where 50nm and 600nm films on STO and NGO show almost identical

high temperature conductivities. This indicates that the high temperature conductivity was not affected by either strain or dislocation content. The dependence of  $\sigma$  on  $p\text{O}_2$  is given in the inset of Figure S1;<sup>1</sup>  $\sigma$  is affected by a change in the carrier concentration with  $p\text{O}_2$ . The carrier population lies in a transition between being controlled by the Sr-doping and by cation vacancies related to gas phase oxidation.<sup>2-5</sup> In general, our films were consistent with reports on bulk LSM with a thermal activation energy of  $E_a \approx 0.1$  eV.<sup>2</sup> These results indicate that the defect behavior and electron transport in all films are similar to bulk LSM (and each other), and that differences in  $k_{chem}$  should not be related to differences in the steady state conductivity values.



**Figure S2.** Steady state conductivity as a function of temperature for 50 nm and 600 nm films on STO (100) and NGO (110). Inset shows the steady state conductivity as a function of oxygen partial pressure of 600 nm LSM film on STO (100).<sup>1</sup>

### $k_{chem}$ for oxidation and reduction processes

Figure S3 plots  $k_{chem}$  measured at 600 °C, during both oxidation and reduction (of the  $p\text{O}_2$  between 500 and 50 mTorr) as a function of film thickness  $t$  (as  $\log k_{chem}$  vs.  $t$ ). For most films, no difference was observed between oxi-

duction and reduction (except the 50nm film on NGO).  $k_{chem}$  values during oxidation and reduction processes for films on STO and NGO are given in the inset. Note that  $k_{chem}$  is a function of substrate (s) and thickness.  $k_{chem}$  for films on STO are always larger than  $k_{chem}$  on NGO. In principle, the surface exchange coefficient should be independent of thickness,<sup>6</sup> but clear and strong deviations from a thickness independent value are observed as the thickness decreases. The thickness where the constant  $k_{chem}$  value is obtained depends on substrate, where for films on STO,  $t \approx 100$  nm; for films on NGO,  $t \approx 200$  nm. All data reported and analyzed in this manuscript were for the reduction process.

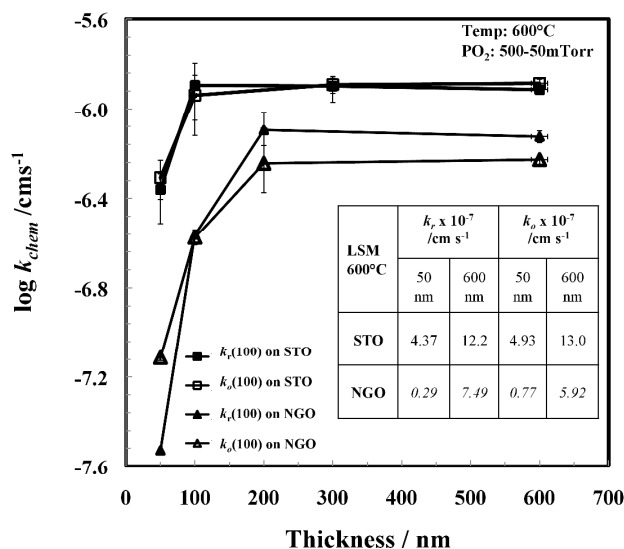


Figure S3. Surface exchange coefficients of 50 nm to 600

nm films on STO (100) and NGO (110) as a function of film thickness during both oxidation ( $k_o$ ) and reduction ( $k_r$ ) processes.

## REFERENCES

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