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Understanding the role of acidity on the surface exchange reaction in mixed conductors: what is the effect of surface hydration?†

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An increasingly robust body of evidence attests that the kinetics of the oxygen exchange reaction at the surface of mixed ionic–electronic conducting oxides can be modified by infiltrating binary oxides. Furthermore, a clear relationship has been found between the reaction rate and the acidity of the surface binary oxide. Nevertheless, the underlying mechanism is still poorly understood. In this study we investigate the effect of acidic and basic infiltrated species (SiO_2 and CaO) on $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$ (STF), a perovskite-structured, technologically relevant MIEC. From these experiments and an analysis of literature data, we demonstrate that a model based on electron-transfer as the rate-determining step and a modified surface electron concentration is quantitatively inconsistent with the data. Consequently, we propose instead that water species, present at trace levels in the conditions of the experiments, play a decisive role in the surface exchange kinetics and their modification through acidic or basic infiltrated species.

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Introduction

Despite its technological importance, the oxygen surface exchange reaction remains poorly understood for the general class of materials termed mixed ionic–electronic conducting oxides (MIEC oxides). At first sight, this is surprising: the reaction involves only a simple, small molecule and a solid. A deeper consideration reveals that this is not at all surprising: the reaction has a complex and multistep nature, involving the adsorption and dissociation of molecular species, charge transfer to the adsorbates from the solid, and the incorporation of adsorbates into the oxide lattice.[1] For MIEC oxides, the concentration of reaction intermediates and the rate-determining step (RDS) remain elusive or controversial.[2] This lack of understanding hinders the design of mixed conducting oxides with superior surface exchange rates.

In response to the complexity and multistep nature of the reaction, researchers have devoted efforts over the last few decades to developing empirical correlations between the surface exchange rate and material properties that are easier to measure or calculate, with the ultimate aim of tailoring surface exchange rates *via* compositional design. These material properties include the concentration of oxygen vacancies and electrons,[2] the oxygen diffusion coefficient,[3] the bulk oxygen p-band centre or bulk vacancy formation energy,[4] and the gap between the Fermi level and the conduction band.[5] The benefit of correlating these properties to the surface exchange rate is that they are based on bulk properties of the material and, therefore, are easy to measure reliably. Each of these correlations, however, suffer from the same limitation: they are based on the bulk properties of the MIEC rather than on its surface properties. This assumes that there is a simple, unique relationship between the bulk chemistry and the kinetics of the surface reactions, and therefore does not provide any mechanistic insight into the exchange reaction nor does it account for the variability in surface exchange rates observed for nominally the same compositions within the literature.[4]

Recently, the Smith acidity of surface oxides was identified by Nicollet *et al.* as a sensitive descriptor that shows a strong correlation with the surface exchange rate.[6] This descriptor has the clear benefit of being based on surface chemistry rather than bulk properties. Specifically for Pr-substituted ceria (PCO), Nicollet *et al.*[6] demonstrated that binary oxides infiltrated onto the surface modified the surface exchange rate, k_{chem}, by up to 5 orders of magnitude. The change in k_{chem} was correlated with the acidity of the infiltrated oxide: oxides that are more basic than PCO (Gd_2O_3, CaO, Li_2O) led to an increase in k_{chem}, while oxides that are more acidic (Al_2O_3, SiO_2) led to a decrease. Furthermore, despite such a large change in k_{chem}, no change was observed in the activation energy, E_A, strongly implying no change in the mechanism of the surface exchange reaction.

Since Nicollet *et al.*[6] proposed the link between surface acidity and the oxygen exchange rate, there have been numerous corroborating studies. Riedl *et al.*, for example,

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experimentally reproduced the same effect, which was initially shown using porous ceramics, on freshly fabricated surfaces of PCO thin films using *in situ* pulsed laser deposition (iPLD).[7] Several studies have reproduced similar effects in perovskite-structured $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC).[8–11] Furthermore, in a survey of the literature, it was shown that the surface exchange rate correlates with the Smith acidity for the native surfaces of the perovskite- and double perovskite-structured cobaltates ($LaCoO_3$, $La_{0.6}Sr_{0.4}CoO_{3-\delta}$, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$, $PrBaCo_2O_{5+\delta}$ and $GdBaCo_2O_{5+\delta}$).[12] In addition, the concept of acidity has also been used to explain a long-standing controversy regarding the effect of Sr-compounds on the surface exchange of LSC: at higher temperatures SrO, a basic oxide improves the surface exchange, while at low temperatures it forms acidic $SrSO_4$ and $SrCO_3$ phases which reduce the exchange rate.[13] Finally, it has been demonstrated that successive infiltration of basic species is effective at recovering surfaces after degradation from poisons on high temperature devices such as silica and chromia.[14–17]

These reports highlight the significance of having a strong correlation between a readily available descriptor of the surface chemistry and the surface exchange rate. It can be used to explain inconsistencies in experimental datasets caused by the presence of common surface contaminants (SiO_2, Cr_2O_3, CaO, Al_2O_3, CO_2, SO_4), and it constitutes a largely unexplored route for designing new MIEC materials for electrochemical devices, with superior surface exchange rates and chemical stability. While current experimental evidence for this correlation is robust, the underlying mechanism that links the acidity to the exchange rate is unclear.

The mechanism proposed by Nicollet *et al.* assumes electron transfer as the RDS and requires the degree of band bending at the surface of the MIEC to vary, owing to a pinning of the Fermi level to that of the binary oxide on the surface.[6] For basic oxides, the bands of the MIEC oxide bend downwards leading to an accumulation of surface electrons, while for acidic oxides, the bands bend upwards leading to a depletion of electrons. This picture was found to be in qualitative agreement with the experimental data.

In this study, we examined the role of acidity on the surface exchange rate of $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$ (STF). STF was selected as a model system to study because (1) it is a technically relevant perovskite structured MIEC,[18,19] (2) a point-defect model of the bulk is well established,[20] and (3) electron transfer has been reported as the RDS from several independent studies.[5,21–23] We measured the surface exchange rate, k_{chem}, of porous STF using electrical conductivity relaxation (ECR), focussing on the effects of infiltrated basic (CaO) and acidic (SiO_2) oxides. Through these new data, we explore the limitations of the band-bending model, and propose a yet unconsidered effect: that of H_2O-based species on the surface.

Experimental

$SrTi_{0.65}Fe_{0.35}O_{3-\delta}$ powder was prepared by a solid-state route. Commercially obtained precursors, $SrCO_3$ (99.99% purity, Alfa Aesar), TiO_2 (99.995% purity, Alfa Aesar) and Fe_2O_3 (99.999% purity, Acros Organics) were milled in a planetary ball mill (Fritsch Pulverisette 7) in a PTFE container with 5 mm ZrO_2 balls in ethanol for 6 h at 850 rpm. The powder was then dried, uniaxially pressed into pellets, and sintered at 1300 °C for 6 h. The pellets were checked for phase purity by X-ray diffraction (XRD, Bruker D2 Phaser), reground in a ZrO_2 pestle and mortar, and ball milled again under the same conditions. After drying, the powder was sieved to restrict the aggregate size to between 20 μm and 100 μm, uniaxially pressed, and sintered at 1100 °C for 6 h to obtain a porous ceramic body.

XRD measurments were repeated and the resultant patterns refined using the Le Bail method (using the FullProf software) to confirm the phase purity and the cubic perovskite structure in the $Pm\bar{3}m$ space group (ESI, Fig. S1†). The density of the ceramics was calculated to be 70.6% from geometric measurements and the refined lattice parameter (3.902 Å) from XRD. The average and distribution of grain sizes was determined by scanning electron microscopy (SEM; JSM-7800F, JEOL, Japan) to be (0.53 ± 0.32) μm (ESI, Sections 2 and 3†). X-ray energy dispersive spectroscopy (XEDS; Oxford Instruments) confirmed the desired stoichiometry had been obtained (ESI, Table S1†).

In preparation for electrical conductivity relaxation (ECR) measurments, the porous ceramic pellet was sectioned into bar shaped samples using a diamond wire saw (4240, Well Diamond Wire Saws, Germany) with dimensions of approximately 2 mm × 3 mm × 20 mm. The surfaces of the bars were lightly sanded with 800 grit SiC paper to remove blemishes and then cleaned for 10 min in an ultrasonic bath of ethanol, followed by acetone, and then ethanol again. Four gold wire contacts were wrapped around each bar sample, painted lightly with gold paste (Heraeus, Germany), and sintered at 800 °C for 2 h to ensure good connectivity. All samples were cut from the same ceramic pellet to minimise any variability in surface contamination and in microstructure.

CaO and SiO_2 binary oxides were infiltrated into the porous bars using solutions of $Ca(NO)_2 \cdot 4H_2O$ (99%, Emsure) dissolved in ethanol and tetraethoxysilane (99.9% Alfar Aesar), respectively. The STF samples were infiltrated with 0.5 at% of the respective cations. This was done using ≈60 μL of a 0.2 mol L^{-1} solution for a sample mass of ≈0.4 g. Prior to measurement using ECR, the infiltrated samples were calcined within the tube furnace of the ECR set-up at 625 °C under p_{O_2} of 0.1 atm for 1 h to form the infiltrated oxide.

ECR measurements were performed in a tube furnace within a quartz tube under a flowing gas atmosphere. The sample temperature was monitored by an S-type thermocouple located adjacent to the sample. Once the sample temperature was considered sufficiently stable, the p_{O_2} was rapidly changed from 0.2 atm to 0.1 atm (or *vice versa*) using a bank of mass flow controllers and a four-way valve. High purity O_2 and N_2 gases (5.0 purity, Westfalen) were used, and the total flow rate kept to 50 sccm. For measurments under nominally dry conditions, gases were used directly from the cylinders. For measurement under wet conditions, the water vapour pressure in the atmospheres was controlled by bubbling the gases through two temperature-controlled reservoirs after mixing. Each mixture is oversaturated in the first reservoir and then set to the desired

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water vapour pressure in the second. The gas lines containing humidified gases were heated to prevent condensation. The resistance of the samples was monitored using a source meter (Keithley 2611B) operating in a four-wire galvanostatic mode while ensuring the voltage across the sample did not exceed 0.5 V.

Results and discussion

The surface exchange coefficient k_{chem} of porous STF was measured as a function of temperature from electrical conductivity relaxation (ECR) experiments between oxygen partial pressures of 0.2 and 0.1 atm. Due to the high porosity (29.4%) and small average grain size (0.53 μm) of the samples [see the ESI, Section 3†], the conductivity relaxation can be considered entirely surface limited and fitted to directly extract k_{chem} (ESI, Section 4†), as previously demonstrated for mixed ionic–electronic conducting oxides.[6,24]

Small, systematic differences in k_{chem} were observed between oxidising and reducing steps in p_{O_2} (ESI, Fig. S6†), as expected (because the data refer to the final p_{O_2}), and here an average of these values is presented. All measurements were made for both decreasing and increasing temperature to ensure reversibility, and all samples were measured prior to any infiltration to ensure repeatability and establish a consistent baseline for the unmodified STF surface. k_{chem} for the unmodified STF was found to agree well with literature values (ESI, Fig. S7†).

After assessing k_{chem} of the unmodified STF surface, the samples were infiltrated with 0.5 at% of either a basic oxide, CaO, or an acidic oxide, SiO_2. Fig. 1a compares k_{chem} values obtained for the unmodified and infiltrated surfaces. CaO infiltration led to a 5.2 times increase in k_{chem}, while SiO_2 infiltration led to a decrease to 0.35 of that of the unmodified surface, together altering the surface exchange rate by over an order of magnitude. As shown on Fig. 1b, the activation energy, E_A, remains essentially constant within experimental uncertainty, while the pre-exponential displays a clear trend with the Smith acidity of the surface species. These findings are consistent with those previously reported for PCO.[6,15] Systematic changes in the conductivity of the samples with the acidity were also observed (ESI, Fig. S9†), also consistent with previous work.[6]

We now compare our data with literature values[25] for STF. To do so, we need to convert our chemical exchange coefficients to tracer exchange coefficients using the thermodynamic factor for oxygen, (ESI, Section 6†) which was calculated from the defect-chemical model.[20] In Fig. 2a we find very good agreement between our data and literature data in terms of activation enthalpy, with the absolute magnitude of k_s^* being a factor of 5–8 times higher (which may be due to an overestimated surface area in our case). Importantly, one finds that the data fall on the low-temperature branch of the surface exchange data. For many oxides,[25–31] a change in the activation enthalpy of surface exchange, from a higher value at higher temperatures to a lower value at lower temperatures, is observed. In Fig. 2b and c we reproduce surface exchange data for the MIEC systems, LSCF and CGO, that show this behaviour. In this way, we show that

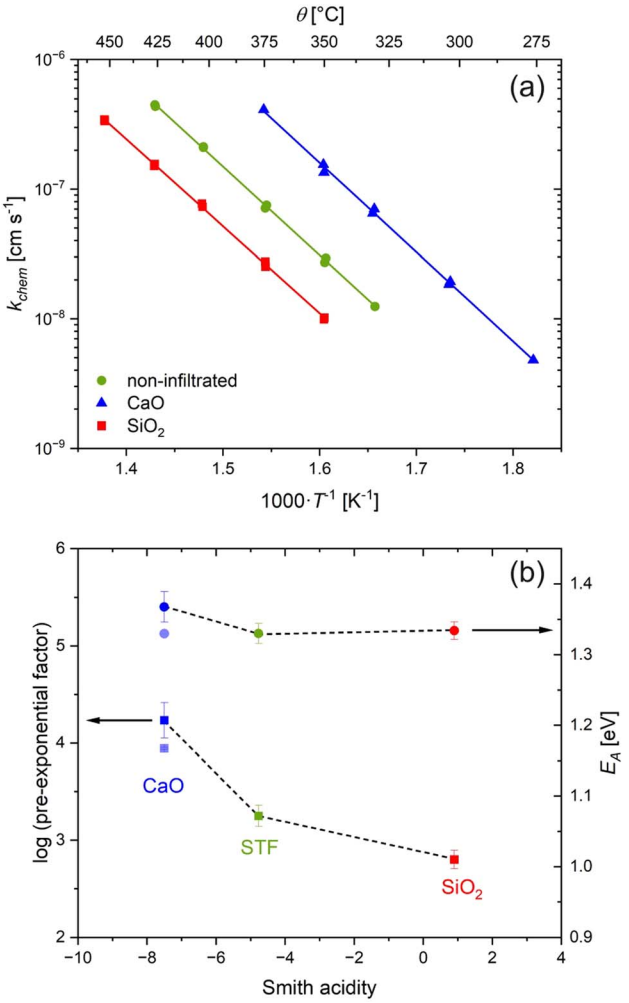


Fig. 1 Influence of acidic and basic species on the oxygen surface exchange coefficient, k_{chem}, of STF measured by ECR. (a) k_{chem} as a function of temperature. The error on k_{chem} are smaller than the data points. (b) Pre-exponential (squares) and E_A (circles) as a function of the Smith acidity of the infiltrated species or uninfiltrated surface. The semi-transparent points indicate the pre-exponential if E_A is kept constant.

our STF data are consistent with literature data for the same system, and generally consistent in terms of the overall surface exchange behaviour of MIEC oxides.

Limitations of the electron transfer model

The findings presented here, and in recently published works,[6–8,10,12–15] represent an increasingly robust body of experimental evidence correlating the Smith acidity of surface species to the surface exchange rate. What is less certain, is the underlying mechanism that is responsible for this empirical relationship. To explore this further, we consider, as Nicollet *et al.* did,[6] that the tracer surface exchange coefficient for semiconducting oxides, such as STF and PCO, can be described by:[2]

$$k_s^* = d_t \nu_0 \sqrt{a_{O_2}} \frac{\left[e_s'\right]\left[s_{ad}\right]}{\left[O_b\right]} e^{-\left(\Delta G_t^{\ddagger} + \Delta G_{ad}\right)/k_B T} \quad (1)$$

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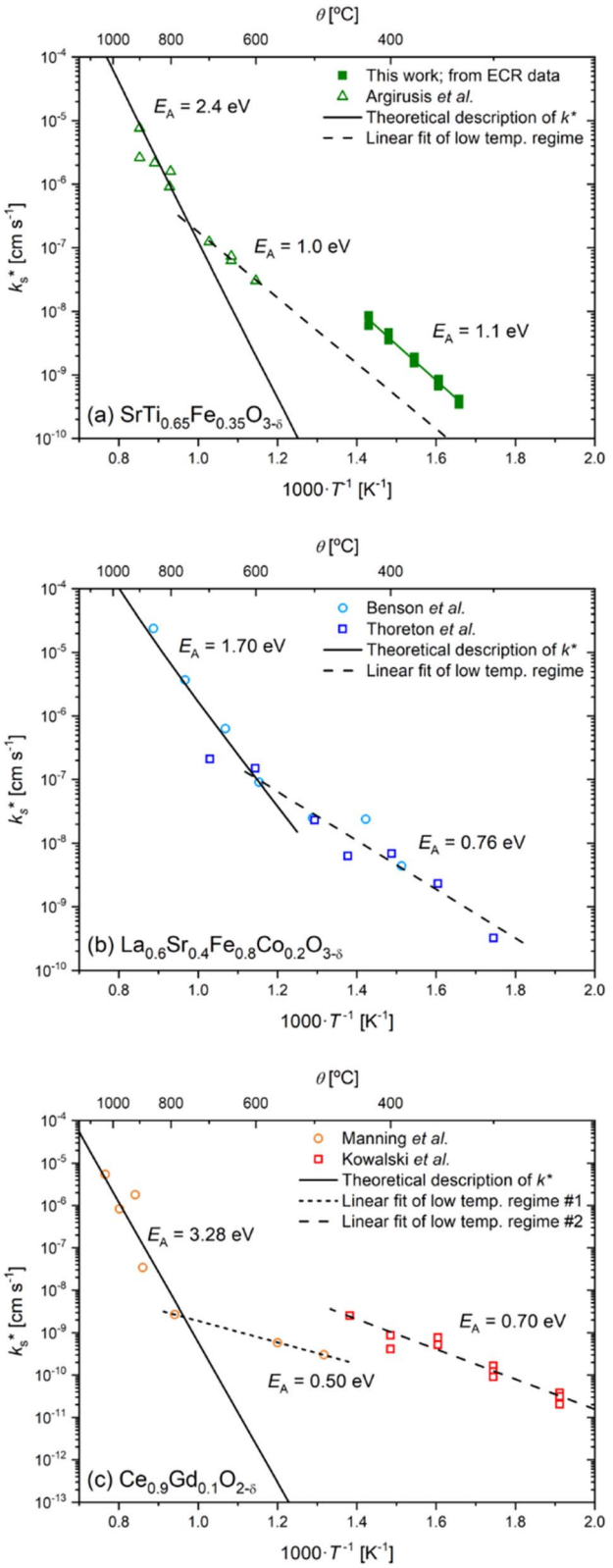


Fig. 2 Tracer surface exchange coefficients for (a) $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$,[25] (b) $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$,[26,27] and (c) $Gd_{0.1}Ce_{0.9}O_{2-\delta}$.[28,29] The open symbols are taken from ^{18}O tracer diffusion measurements in the literature, the solid lines are theoretical descriptions using eqn (1), and the dashed lines are linear fits of the low temperature regimes. In (a) the closed green squares are taken from ECR measurements in this study and converted to k^* using a thermodynamic factor (see ESI, Section 6†) and the dashed line is a fit to the low temperature data by Argirusis *et al.*[25]

This expression assumes the rate-determining step (RDS) is electron transfer from the conduction band at the surface of the oxide to an adsorbed oxygen species, as expected to be the case for STF.[5,21,22] d_t is the distance over which the electron transfer takes place, ν_0 is the attempt frequency, and a_{O_2} is the oxygen activity. $[e_s']$, $[s_{ad}]$, and $[O_b]$ are the site fractions of electrons at the surface, of surface adsorption sites, and of oxide ions in the bulk, respectively. $\Delta G_t^{\ddagger}$ is the Gibbs activation energy for electron transfer, which could either be the difference in the energy barrier between the conduction band and the adsorbed oxygen Fermi level, or an activation barrier that must be overcome. ΔG_{ad} is the Gibbs energy of oxygen adsorption from the gas onto an adsorption site.

From experimental data (obtained in this study and in other studies[6,7]), the change in k_s^* upon infiltration clearly originates from the pre-exponential terms, which has been shown to change in magnitude over a range of $\sim 10^1$ for STF and $\sim 10^5$ for PCO with the acidity of the surface species. As it seems unlikely that the distance, attempt frequency, oxygen activity, or bulk oxygen concentration could be varied by such an amount at the surface, attention naturally turns to the surface electron concentration and the concentration of (suitable) adsorption sites.

Drawing on the equivalence of Smith acidity and position of the Fermi level for oxides,[32] Nicollet *et al.* postulated that pinning of the Fermi level and band bending at the surface cause an accumulation/depletion of electrons in the form of a space-charge zone.[6] The site fraction of electrons at the surface, $[e_s']$, can be related to the degree of band bending, *i.e.* the space-charge potential ϕ_0, through a Maxwell–Boltzmann expression,

$$\left[e_s'\right] = \left[e_b'\right] \exp\left(\frac{e\phi_0}{k_B T}\right) \quad (2)$$

and in turn ϕ_0 is equal to the offset between the Fermi levels of the MIEC oxide and of the infiltrated species (ESI, Fig. S10†). This hypothesis has two major strengths. First, it establishes a relationship between the Smith acidity and the surface exchange coefficient that describes the increase or decrease with basic or acidic species, respectively. Second, the space-charge potentials necessary to alter the surface exchange rate over a range of $\sim 10^5$ are of the order of ± 0.5 eV for the investigated temperature range, which one could reasonably expect to be present at an oxide surface.

Despite these strengths, we argue that this model is not indicative of the underlying mechanism based on three observations. (1) The model predicts that E_A should increase with acidic species and decrease with basic species (ESI, Section 6†), yet in this work and in the literature the activation energy remains constant within experimental error. (2) Riedl *et al.* reported XPS studies on the surface of PCO films with a basic oxide coating that did not show any increase in the concentration of Pr^{3+} species, which would be expected if electron

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accumulation due to band bending was occurring.[7] (3) In terms of the activation energy, our data for STF (1.1 eV) agrees very well with literature data for STF (1.0 eV), as published by Argirusis *et al.*,[25] for the low-temperature regime. It is, however, the high-temperature regime (>700 °C) that can be well described with eqn (1) (see Fig. 2a), *i.e.* with a model assuming electron transfer to be the RDS. $[e'_s]$ and $[O_b]$ are taken from the defect model,[20,33] and the $e^{-(\Delta G_t^{\cdot}+\Delta G_{ad})/k_BT}$ term, expanded to $e^{-(\Delta S_t^{\cdot}+\Delta S_{ad})/k_B}e^{-(\Delta H_t^{\cdot}+\Delta H_{ad})/k_BT}$, can be well described with the standard $\Delta S_t^{\cdot} + \Delta S_{ad} = -4k_B$ and a fitted $\Delta H_t^{\cdot} + \Delta H_{ad}$ of 0.9 eV, which is reasonable considering the value for weakly acceptor doped STO (1.15 eV).[2] Hence, our data evidently does not refer to the regime in which electron transfer is supposedly the RDS and to which band bending can affect the availability of electrons. As we argue in the next section, there is evidence to suggest that the dominant mechanism responsible for surface exchange in the 'low' temperature section involves water species from the gas atmosphere.

Case for water species

Eqn (1) has been shown to describe k_s^* quantitatively as a function of T and p_{O_2} for diverse MIEC systems, including acceptor-doped $SrTiO_3$, $Gd_{0.1}Ce_{0.9}O_{1.95}$, and $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$.[2] In each case, it was shown that the literature data could only be described by eqn (1) above a certain temperature, T_{trsn}, below which the activation energy decreases and k_s^* is observed to be larger than that predicted by eqn (1), as shown for $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ and $Gd_{0.1}Ce_{0.9}O_{1.95}$ in Fig. 2b and c, respectively. This trend is also reproduced in the STF system, as shown in Fig. 2a. Such a change in the activation energy is indictive of a change in the RDS within a mechanism or a change to a different dominant mechanism.

It has been argued previously that the change in activation energy is caused by the presence of adsorbed water, possibly in the form of surface hydroxyl (OH) species, due to trace amounts of water vapour in gases used in tracer experiments.[2,34] Support for this hypothesis comes from multiple studies where oxygen exchange has observed to be faster in the presence of H_2O.[35–37] This argument has been strengthened by tracer diffusion data for weakly acceptor-doped STO single crystals exchanged under either nominally dry or wet atmospheres. Kler *et al.* observed higher exchange rates and lower activation energies for wet atmospheres, which converged with the data under nominally dry atmospheres at higher temperatures.[38]

We propose, based on these arguments and on the limitations of the electron-transfer model, that trace amounts of water vapour in the gas atmosphere during our experiments, and potentially previous studies on PCO,[6,7] play a decisive role on the surface exchange kinetics. It may be expected that removing the trace amounts of water from the gas atmosphere would result in a lower k_s^* and higher activation energy, which would be consistent with the data at high temperature and indicative of electron transfer being the RDS. It is important to note, however, that a transition between high and low temperature regions has been observed even when the water partial pressure in the gas atmosphere is very low. Kler *et al.* performed isotope exchange experiments on (110) and (111) oriented STO single crystals, where the H_2O partial pressures (p_{H_2O}) was kept below 1 × 10^{-8} bar and observed a transition between high and low temperature regions with T_{trsn} = 737 °C.[30] It would be, therefore, extremely challenging to dry gases beyond this level for ECR experiments.

From Fig. 2, one might expect that any measurments of the surface exchange below 700–500 °C to fall within this low temperature regime, unless the atmosphere is kept exceptionally dry. To investigate this hypothesis further, we performed ECR measurments on STF under varying p_{H_2O}. Due to the challenge of experimentally drying gases to below ppb levels, we instead opted to increase the p_{H_2O} above our nominally 'dry' conditions. The clearest indication that water in the gas atmosphere alters the exchange kinetics would be a shift in T_{trsn} to

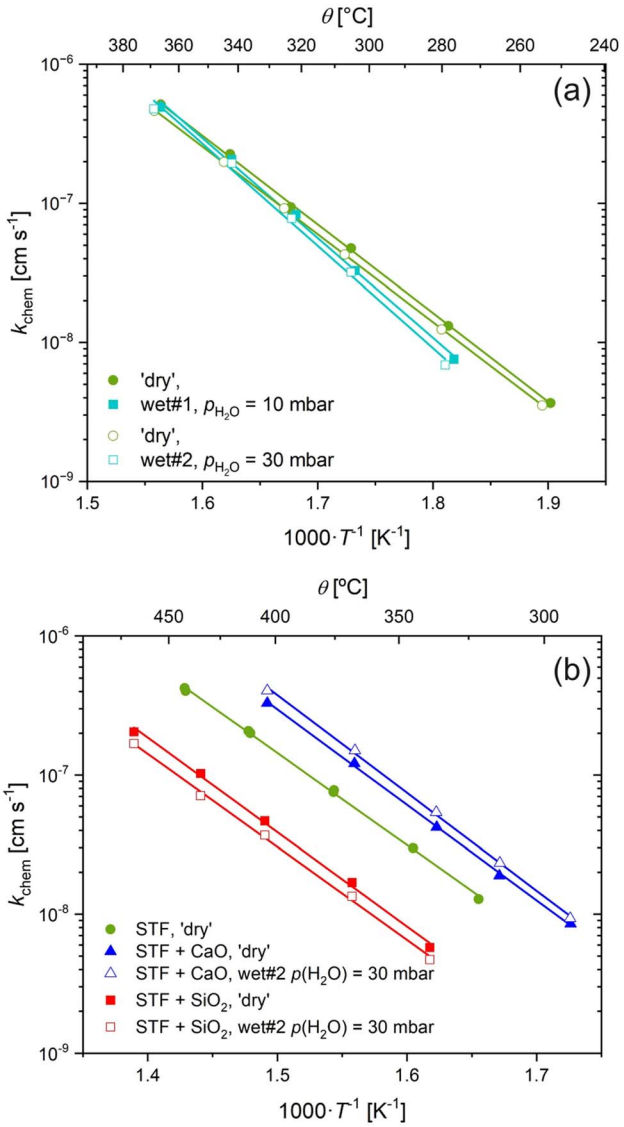


Fig. 3 Oxygen surface exchange coefficent, k_{chem}, of STF measured by ECR under 'dry' and wet conditions. (a) Uninfiltrated STF for nominally dry gas and under wet atmospheres. (b) Influence of acidic and basic species on k_{chem} under 'dry' and wet conditions.

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lower temperatures at higher p_{H_2O}. Unfortunately, the range of temperatures that we can perform ECR measurments is limited because the relaxation becomes too fast at high temperatures to accurately monitor with our setup.

Fig. 3a shows k_{chem} of non-infiltrated STF measured under three conditions: 'dry' (p_{H_2O} unknown), wet#1 ($p_{H_2O} = 10$ mbar), and wet#2 ($p_{H_2O} = 30$ mbar). Only minimal changes were observed for k_{chem} comparing between all three conditions. These deviations between nominally 'dry' and the two wet conditions are larger with decreasing temperatures, resulting in a small, albeit repeatable, change in the activation energy from (1.25 ± 0.02) eV to (1.45 ± 0.06) eV. This may be due to hydration of the bulk, resulting in a change in the sub-surface oxygen vacancy and electron concentration, rather than just hydroxylation of the surface.

An increase in the magnitude of k_{chem} and a substantial decrease in the activation energy would be expected if there was a change in mechanism from electron transfer under 'dry' conditions to one involving water species under wet conditions. It is, however, clear from the data in Fig. 3a, that this is not what is observed. This suggests either that there is no effect or that water is dominating oxygen surface exchange in our ECR measurements in all conditions, including the 'dry' conditions, such that an increase in p_{H_2O} does not lead to change in the surface water species involved in the surface exchange reaction, as the surface sites are saturated at all levels of p_{H_2O} investigated.

To further investigate the role of water species on the surface exchange reaction with infiltrated acidic/basic species, we repeated the ECR measurements on STF before and after infiltration with a basic oxide, CaO, and an acidic oxide, SiO_2 under 'dry' and wet conditions. The resultant k_{chem} values are shown in Fig. 3b. Under wet conditions, the basic and acidic species still lead to dramatic increases and decreases in the surface exchange reaction, respectively. The magnitude of the change is approximately the same, or even slightly higher under wet atmospheres compared to 'dry', although this may be within the experimental uncertainty. It is clear from these results that the mechanism by which acidic/basic infiltrated species lead to dramatic changes in the surface exchange reaction plays a decisive role in wet conditions as well as in 'dry' conditions.

Thus, on the one hand, our k_s^* data falls on the low-temperature branch, strongly suggesting a different mechanism to that operative for the high-temperature branch, which we can describe using the electron transfer model. Furthermore, the presence of trace amounts of water has been heavily implicated in the change from high-temperature to low-temperature branch.[34,38] On the other hand, no significant effect of varying the p_{H_2O} on k_{chem} were observed (Fig. 3), which may seemingly contradict the hypothesis that water is playing a role in the surface exchange. This does not, however, present a logical inconsistency, as it is important to note that water is present in all conditions, including the nominally 'dry' conditions, and that there is a finite number of surface sites where absorption may occur, resulting in surface saturation at very low p_{H_2O}. Such Langmuir-type behaviour, where the equilibrium fractional surface coverage is unity over a broad pressure range if the adsorption rate is sufficiently high, has been shown for adsorbed water on Y_2O_3-doped ZrO_2 and Al_2O_3 by Raz *et al.*[39] They concluded that a full surface coverage of water species would be present on most oxides below ~450 °C.

Although we cannot at this stage comment on the mechanism, it is not unreasonable to consider that water may be playing a role in the surface exchange. At low temperatures, such as those used in the present study, there are numerous studies demonstrating faster oxygen exchange when H_2O is present in the gas atmosphere. In some examples, it has been shown that oxygen exchange happens faster from H_2O than molecular oxygen,[40–42] while other work has shown that the presence of water may assist in the exchange of molecular oxygen.[43,44]

It is clear that the surface exchange is still strongly affected by the acidity on an infiltrated species under these wet conditions. As discussed above, we argue that a rate-determining step involving electron transfer, as described by eqn (1) and where the electron concentration is modified by the acidity of the surface species according to eqn (2) is not indicative of the underlying mechanism. Instead, the presence of acidic or basic oxides on the surface may shift the adsorption/desorption equilibrium of oxygen and water species (O_2, O, H_2O, OH) on the surface. Recent work by Siebenhofer *et al.* support this line of reasoning. They performed a combination of experimental and computational studies on PCO and LSC showing that the acidity, which they also correlate to the ionic potential, of infiltration or adsorbed species modifies the energy of adsorbed O_2^{-2} and O_2^{-1} species, which is caused by a change in the surface dipole.[10] In the work by Siebenhofer *et al.* the absorption of water species was not considered, but here we argue that considering that in the temperature range being investigated, surfaces are almost certainly hydrated and that H_2O offers a competing pathway for oxygen exchange, this may have an effect or even play a decisive role.

Conclusions

We have investigated the role of acidic and basic oxides on the oxygen surface exchange of STF as a model MIEC. We have reproduced the previously reported effect of infiltrated acidic/basic species on STF under both nominally dry and wet conditions, demonstrating a total change in the surface exchange kinetics of one order of magnitude. Through our experiments and an analysis of the literature data, we reason that a model considering a change in the surface electron concentration is insufficient to describe the underlying mechanism. We instead propose that the presence of water species in the gas atmosphere, which has so far been overlooked, may act as a critical factor in the exchange kinetics, and their interaction with acidic/basic surface species may be the cause for the substantial changes seen in reaction rates.

Data availability

The data supporting this article have been included as part of the ESI.†

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Conflicts of interest

There are no conflicts to declare.

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