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# Reactivity of Perovskites with Water: Role of Hydroxylation in Wetting and Implications for Oxygen Electrocatalysis

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ABSTRACT Oxides are instrumental to applications such as catalysis, sensing, and wetting, where the reactivity with water can greatly influence their functionalities. We find that the coverage of hydroxyls (\*OH) measured at fixed relative humidity trends with the electron-donor (basic) character of wetted perovskite oxide surfaces. Using ambient pressure X-ray photoelectron spectroscopy, we report that the affinity toward hydroxylation, coincident with strong adsorption

energies calculated for dissociated water and hydroxyl groups, leads to strong H-bonding that is favorable for wetting while detrimental to catalysis of the oxygen reduction reaction (ORR). Our findings provide novel insights into the coupling between wetting and catalytic activity and suggest that catalyst hydrophobicity should be considered in aqueous oxygen electrocatalysis.

## INTRODUCTION

The interaction of oxides with water plays a critical role in a large number of applications,<sup>1-5</sup> including water purification, gas sensing and separation, photoelectrochemistry, electrocatalysis, and wetting. The solid/liquid interface between water and oxides is one of the fundamental components in electrochemistry and electrocatalysis. The hydroxylation and binding of surface adsorbates<sup>6-7</sup> on oxides can greatly influence the adsorptive and wetting properties<sup>4-5, 8-9</sup> and catalytic activity.<sup>10-14</sup> These observations have been rationalized by the change in polarity induced by surface hydroxyl species.<sup>8, 13</sup> Here we evaluate intrinsic properties of oxide surfaces that can bridge wetting and activity for oxygen electrocatalysis.

Directly measuring hydroxylation and surface adsorbates in liquid water and correlating these species to wetting and catalytic activity is challenging – particularly for oxide systems where both the adsorbate and catalyst contain oxygen. Conventional contact angle measurements do not provide information at the molecular level on water adsorption energetics, the degree of hydroxylation, or interfacial hydration structure.<sup>15</sup> On the other hand, the molecular interaction of water with complex, catalytically active metal oxide surfaces has been studied using traditional surface science microscopy and spectroscopy techniques but only in ultra-high vacuum and often at cryogenic temperatures.<sup>16-18</sup> Here we take advantage of recent advances in ambient pressure X-

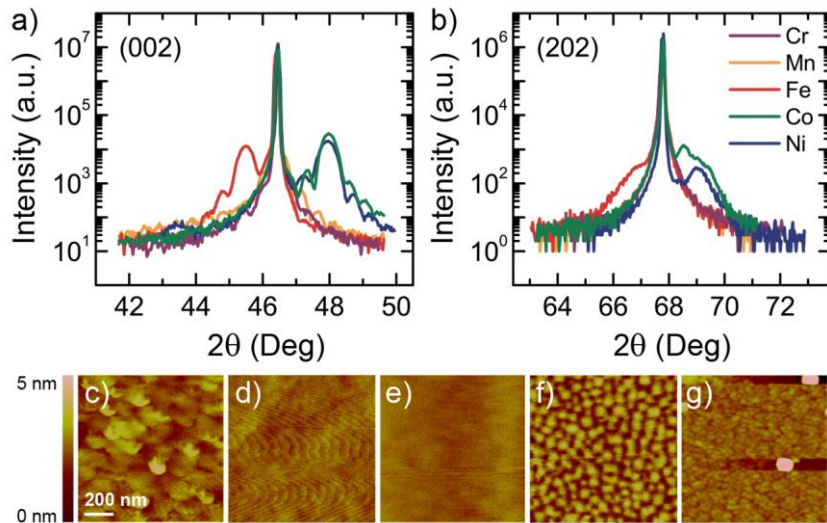
ray photoelectron spectroscopy (AP-XPS)<sup>19-21</sup> to measure the extent of surface hydroxylation and adsorption of water on oxide surfaces.

In this report, we utilize the flexibility of the perovskite surface chemistry ( $\text{LaMO}_3$ ,  $M = \text{Cr}$  to  $\text{Ni}$ ) to show that increasing hydroxylation measured from AP-XPS scales with increasing hydrophilicity from contact angle measurements. Both hydroxylation and surface electron-donating character exhibit a W-shape as a function of  $d$  electrons, which is in agreement with computed energetics of hydroxylation on  $\text{MO}_2$ - and  $\text{LaO}$ -terminated surfaces from density functional theory (DFT). Moreover, decreasing surface hydrophilicity correlates with increasing catalytic oxygen reduction reaction (ORR) activities in basic solution.

## EXPERIMENTAL AND THEORETICAL METHODS

**Thin film growth and characterization.** Films were fabricated by pulsed laser deposition (PLD) on single crystal (001)-oriented 0.5 wt% Nb-doped  $\text{SrTiO}_3$  substrates with a dimension of  $10 \times 5 \times 0.5$  mm (Crystec, GmbH). The PLD targets of  $\text{LaMnO}_3$  and  $\text{LaFeO}_3$  were purchased (Praxair, Inc.) for thin film deposition. The  $\text{LaCoO}_3$  PLD target was synthesized using a solid-state reaction from stoichiometric mixtures of  $\text{La}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$  (Alfa Aesar, USA) and sintered at  $1450^\circ\text{C}$  to 90% theoretical density.  $\text{LaCrO}_3$  and  $\text{LaNiO}_3$  PLD targets were synthesized by glycine-nitrate combustion reaction. Stoichiometric quantities of nitrate precursors –  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.999% metal basis, Alfa Aesar),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99.999% metal basis, Sigma Aldrich) or  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (99.99% metal basis, Sigma Aldrich) – were dissolved in Milli-Q water ( $18 \text{ M}\Omega \cdot \text{cm}$ ), to which glycine was added. The mixture was heated and allowed to slowly evaporate, then heated at  $400^\circ\text{C}$  under air atmosphere for 4 hours. The resulting powder was ground, pressed, and sintered at  $800^\circ\text{C}$  under air atmosphere for 12 hours. The resulting pellet was then re-ground, pressed, and sintered a second time at the same condition.

PLD was performed using a KrF excimer laser ( $\lambda = 248$  nm) at a pulse frequency of 10 Hz and laser fluence of  $\sim 1.50$  J cm<sup>-2</sup>.  $\sim 20$  nm films were deposited of LaCrO<sub>3</sub>, LaMnO<sub>3</sub>, LaFeO<sub>3</sub>, LaCoO<sub>3</sub>, and LaNiO<sub>3</sub> under the conditions shown in **Table S1**. Thin film X-ray diffraction (XRD) was performed using a four-circle diffractometer (Bruker D8, Germany) in normal and off-normal configurations (**Figure 1 a, b**), with relaxed lattice parameters and associated strain in **Table S2**. The film thickness was estimated using the thickness fringes in the high-resolution  $\theta$ - $2\theta$  scans of the (002) diffraction peaks (“Epitaxy” software, Panalytical). Film surface morphologies were examined by atomic force microscopy (AFM, see **Figure 1 c-g** and **Table S3**) (Veeco), with root-mean-square (RMS) roughness values  $\leq 0.5$  nm, except for LaNiO<sub>3</sub> (1.6 nm). Some particles were observed on the LaNiO<sub>3</sub> surface, the coverage of which was estimated from 100 $\times$  optical microscopy images to be  $<3.3\%$ . These particles are expected to be stoichiometric LaNiO<sub>3</sub> fragmented from the target during deposition,<sup>22</sup> and the difference in surface area compared to a flat one is  $<1.9\%$ .



**Figure 1.** Characterization of LaMO<sub>3</sub> films, where  $M =$  Cr (purple), Mn (orange), Fe (red), Co (green<sup>23</sup>), and Ni (blue). High resolution X-ray diffraction (XRD) in the a) normal configuration (002), with thickness fringes indicating high film quality, and b) off-normal configuration (202).

Atomic force microscopy (AFM) of film surfaces and RMS roughness: c)  $\text{LaCrO}_3$  0.4 nm, d)  $\text{LaMnO}_3$  0.2nm, e)  $\text{LaFeO}_3$  0.2 nm, f)  $\text{LaCoO}_3$  0.5 nm,<sup>23</sup> g)  $\text{LaNiO}_3$  1.6 nm. The 200 nm scale bar is the same for all images, and the color scale is 0-5 nm.

**Ambient-Pressure X-ray Photoelectron Spectroscopy (AP-XPS).** AP-XPS was collected at Beamline 11.0.2<sup>23-24</sup> at Lawrence Berkeley National Laboratory's (LBNL) Advanced Light Source (ALS). Films were placed onto a ceramic heater,<sup>25</sup> with a thermocouple mounted directly onto the sample surface for temperature measurements, and isolated from the sample holder clips with an  $\text{Al}_2\text{O}_3$  spacer. A piece of Au foil, scraped clean with a razor, was placed on top of a corner of the sample for calibration of the incident photon energy, referenced to the Au 4f at 84.0 eV. The binding energy (BE) of the oxide O 1s bulk peak was calibrated by defining the C 1s of adventitious carbon present on the sample prior to cleaning at 284.8 eV. All subsequent spectra are aligned relative to this O 1s peak.

Care was taken to reduce the beam flux so issues such as coking were not observed. This was achieved by limiting the dispersive and non-dispersive slits to 15 and 50  $\mu\text{m}$ , respectively, and the X-ray beam shutter was kept closed between scans. The change in coverage of \*OH for a given change of relative humidity (RH) was slightly less comparing amongst fresh regions of the sample versus comparing the change in coverage of \*OH at the same location. However, coverage of \*OH in both cases showed the same saturation behavior with RH,<sup>23</sup> and we report coverage of \*OH only at the most humid condition. We attribute the differences from beam irradiation to an increase in the dissociation constant of  $\text{H}_2\text{O}$ ,<sup>26</sup> effectively reducing the barrier for hydroxylation. Because the irradiation was constant amongst materials and coverage of \*OH shows a saturation-like behavior with RH, we do not expect adverse effects in comparison amongst materials.

The samples were cleaned by heating to 300 °C in  $p(\text{O}_2)$  of 100 mTorr (measured by a calibrated capacitance gauge) until clean of carbon (**Figure S1**). A small amount of  $\text{SO}_x$  species were observed in the  $\text{O}_2$  environment from displacement of residue species from the chamber walls (for an estimation of the contribution to the O 1s spectra, see our previous publication<sup>23</sup>), which reduced to a negligible quantity upon introduction of  $\text{H}_2\text{O}$ . After characterization of the clean surface in  $\text{O}_2$ , the chamber was evacuated to a pressure  $< 1.5 \times 10^{-7}$  Torr, and  $p(\text{H}_2\text{O})$  of 100 mTorr was introduced into the chamber. The  $\text{H}_2\text{O}$  was prepared from deionized water (Millipore,  $>18.2$  M $\Omega$  cm) and degassed by several freeze-pump-thaw cycles. Contaminants in gaseous species have been previously noted to affect wetting,<sup>27</sup> and any possible influence from their presence has been carefully assessed. The sample was then cooled in increments of 25 °C down to a final temperature of 25 °C, keeping the chamber pressure constant at  $p(\text{H}_2\text{O})$  of 100 mTorr. At every temperature, the O 1s and C 1s core level spectra were collected, and at 100 °C increments as well as 25 °C, the La 4d and transition metal 3p core level spectra were also collected. All spectra were taken at an incident energy of 735 eV. The C/O relative sensitivity factor (RSF) was experimentally obtained by measuring the respective 1s core levels of 250 mTorr  $\text{CO}_2$  gas. This provided a value of  $0.86 \pm 0.03:1$  (O 1s:C 1s) for an incident photon energy of 735 eV. This value depends on the experimental geometry, and potentially the chamber pressure and should be measured for each experimental run.

Coverages of surface oxygenated species (**Table S4, S5**) were estimated from the O 1s spectra using a multilayer electron attenuation model,<sup>28-29</sup> as discussed in reference 23. This model takes as an input the oxygen atomic density,  $N$ , the inelastic mean free path (IMFP,  $\lambda$ ), and the photoelectron emission angle. While the coverages of \*OH and \*H<sub>2</sub>O discussed in the text give a more physical comparison amongst materials, the relative differences amongst LaMO<sub>3</sub> materials

can also be seen in the percent contribution of these species to the total O 1s counts in **Table S6**. A small amount of adventitious carbon was also observed at lower temperatures (**Supporting Information, Table S6**), and is assumed to sit atop the surface uniformly and not influence the results.

**Contact Angle Measurements.** Contact angles for the three probe liquids of diiodomethane (DIM, Alfa Aesar), ethylene glycol (EG, Alfa Aesar), and deionized water (18 M $\Omega$ -cm, Millipore) were measured using a Ramé-Hart M500-advanced goniometer. The advancing and receding contact angles were measured by adding/removing water from a 5  $\mu$ l droplet on the surface at the rate of 0.2  $\mu$ l/sec. This ensures that the capillary number is always low enough for accurate measurements. A smaller droplet volume was used with other probe liquids due to the lower contact angle and small sample size. Measurements on a second LaMnO<sub>3</sub> film yielded a water advancing angle within 2° and a receding angle within 5° of that measured on the first film. Repeat measurements on the first film after drying yielded values within the same range.

**Electrochemical Measurements.** Electrical contacts were applied to the back of the conductive Nb-doped SrTiO<sub>3</sub> substrate, as reported previously.<sup>30</sup> Gallium–indium eutectic (Sigma-Aldrich, 99.99%) was scratched into the Nb-doped SrTiO<sub>3</sub>, and a Ti wire (Sigma-Aldrich, 99.99%) was affixed with silver paint (Ted Pella, Leitsilber 200). The back and sides of the electrode, as well as the wire, were covered with a non-conductive, chemically resistant epoxy (Omegabond 101), so only the catalyst surface was exposed to the electrolyte.

Electrochemical measurements were conducted with a Biologic SP-300 potentiostat in an ~120 mL solution of 0.1 M KOH, prepared from deionized water (Millipore, >18.2 M $\Omega$  cm) and KOH pellets (Sigma-Aldrich, 99.99%). Potentials were referenced to a saturated Ag/AgCl electrode (Pine), calibrated to the reversible hydrogen electrode (RHE) scale in 0.1 M KOH. Oxygen



reduction reaction (ORR) measurements were carried out in an electrolyte pre-saturated by bubbling O<sub>2</sub> for at least 45 minutes and under continuous O<sub>2</sub> bubbling (Airgas, ultrahigh-grade purity). ORR cyclic voltammetry (CV) at a scan rate of 10 mV s<sup>-1</sup> is plotted corrected for capacitance by averaging the forward and backward sweeps. Electrical impedance spectroscopy (EIS) was performed at the open circuit voltage with an amplitude of 10 mV. Potentials were corrected for the electrolyte/cell resistance from the high frequency intercept of the real impedance (45 Ω).

**Density Functional Theory Calculations.** Density functional theory calculations with Hubbard U correction (DFT+U)<sup>31-32</sup> were carried out with a periodic approach and plane wave basis set, as implemented in the VASP code.<sup>33-34</sup> Core electrons were described with the Projector Augmented Wave (PAW) method,<sup>35</sup> and the plane wave cutoff was set to 450 eV. We used the gradient-corrected Perdew-Wang 91 (PW91) functional<sup>36</sup> and the optimal effective U values on the transition metal *d* electrons determined by fitting the formation enthalpies of oxides.<sup>37-38</sup>

Full optimizations of bulk perovskite structures for each LaMO<sub>3</sub> (*M* = Cr, Mn, Fe, Co, Ni) were performed using the experimental symmetry at low temperature<sup>39-42</sup> based on the ferromagnetic ordering in order to use a consistent and tractable set of magnetic structures, except for LaFeO<sub>3</sub>, where we considered a G-type anti-ferromagnetic ordering to account for the higher Néel temperature.<sup>39, 43</sup> Internally relaxed pseudocubic 2×2×2 perovskite supercells were then constructed with effective perovskite lattice constants obtained taking the cube root of the normalized volume (per formula unit) of the fully relaxed perovskites. The fully relaxed perovskite bulk coordinates were used as initial atomic positions and for these calculations the reciprocal space unit cell was sampled by a (2×2×2) *k*-point mesh. The (001) orientation of LaMO<sub>3</sub> pseudocubic perovskites is polar, and symmetric seven-layer slab models were employed in order

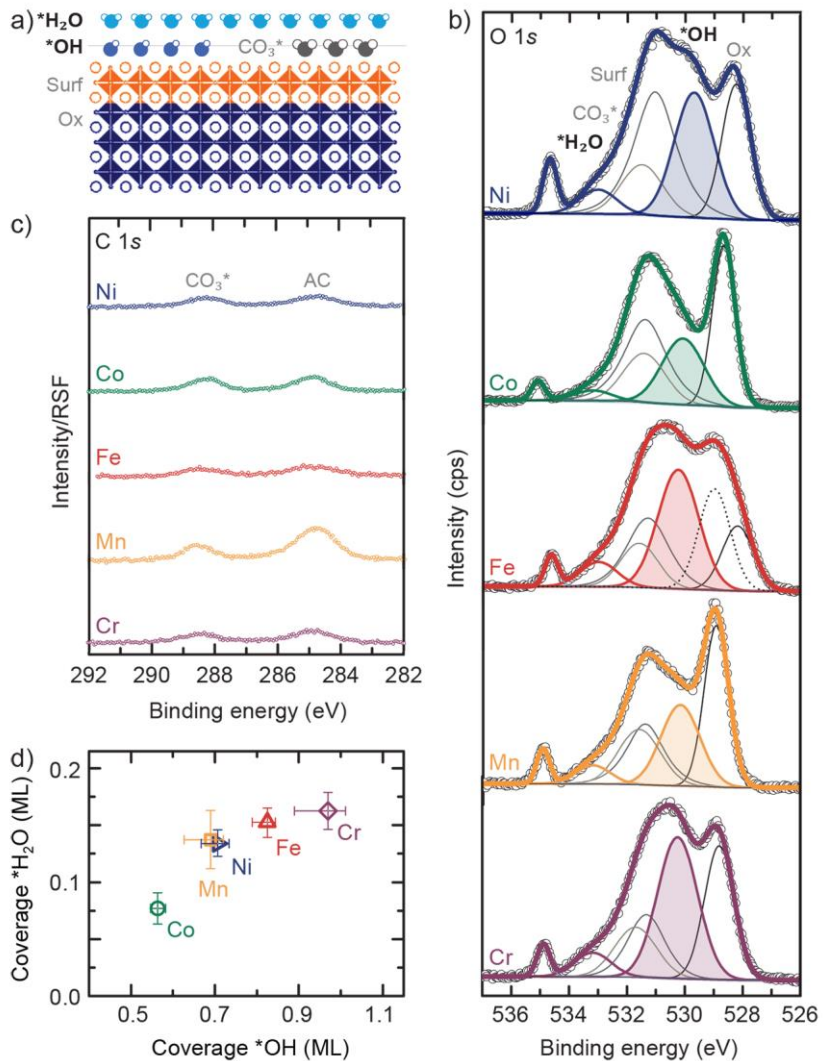
to cancel the related dipole moment perpendicular to the surface. The (2×2) (001) LaO and MO<sub>2</sub>-terminated slab models have been constructed using the 2×2×4 pseudocubic perovskite supercells with 10 Å vacuum space inserted between the two terminations of a (001) slab and removal of an MO<sub>2</sub> layer for the seven-layer (001) LaO slab (and removal of a LaO layer for the seven-layer (001) MO<sub>2</sub> slab). Internal relaxations of the (001) slab coordinates were performed without adsorbates. Previous work has shown that this approach gives a satisfactory description of the surface properties of these systems.<sup>38, 44</sup> The adsorbates (dissociatively adsorbed H<sub>2</sub>O, \*OH, and \*H) were then adsorbed on one side of the slab, and the adsorbate coverage varied from ¼ to 1 monolayer (ML), where 1 ML corresponds to one adsorbate per surface metal atom. The bottom two layers of the slab models were kept fixed, while the adsorbate and remaining slab coordinates were internally relaxed. A (2×2×1) *k*-point sampling was used for such slab models.

Stability of the (dissociatively adsorbed) H<sub>2</sub>O, \*H, and \*OH at the experimental condition was estimated using the chemical potentials of H<sub>2</sub>O, H<sub>2</sub> and O<sub>2</sub> as detailed in the **Supporting Information**. By setting the chemical potential of oxygen to be at the condition of  $T=25$  °C and  $1.5 \times 10^{-7}$  Torr partial pressure of oxygen (the lowest detectable limit in the AP-XPS chamber), and the  $p(\text{H}_2\text{O})$  to be 0.1 Torr, we estimate the corresponding effective applied potential at the experimental condition to be 1.20 V relative to the standard hydrogen electrode (SHE,  $a_{\text{H}^+} = 1$ ). This is comparable to the equilibrium potential of O<sub>2</sub>/H<sub>2</sub>O in O<sub>2</sub>-saturated liquid water for ORR measurements, 1.23 V relative to the reversible hydrogen electrode. The adsorption free energies,  $G_{\text{ad}}$ , were then computed with respect to the H<sub>2</sub>O, H<sub>2</sub>, and O<sub>2</sub> chemical potential references at the effective applied potential of 1.2 V vs. SHE as detailed in the **Supporting Information**.

## RESULTS AND DISCUSSION

### Determining Coverage of OH at Fixed Relative Humidity

We examined the reactivity of water vapor on (001)-oriented  $\text{LaMO}_3$  film surfaces using AP-XPS by performing water isobar experiments to deconvolute the spectra. Quantifying by a multilayer electron attenuation model (**Figure 2 a**), we compare the component species at fixed relative humidity (RH, **Figure 2 b**). The surfaces were cleaned *in situ* by heating in  $\text{O}_2$  (**Figure S1**) before exposure to water vapor. Water isobar measurements ( $p_{\text{H}_2\text{O}} = 100$  mTorr) were performed by cooling, reaching a final RH of  $\sim 0.3\%$  at  $25^\circ\text{C}$ . The O  $1s$  and C  $1s$  spectra of all  $\text{LaMO}_3$  showed similar features (**Figure S2-5**, reference <sup>23</sup>), and the intensities varied with RH. Pronounced changes in the isobar O  $1s$  spectra are noted with increasing RH. This evolution has been discussed in great detail for the case of  $\text{LaCoO}_3$  in reference 23, and we here only summarize the main trends.



**Figure 2.** Quantification of adsorbates by AP-XPS. a) Schematic of the multilayer electron attenuation model used to determine coverages. For further information about the error and deconvolution into bulk “Ox,” surface “Surf,” carbonates “CO<sub>3</sub>\*” and gas phase water, see the Supporting Information and reference 23. b) Fitted O 1s spectra at 25 °C in 0.1 Torr H<sub>2</sub>O. Raw data in counts per second are shown as circles, and the envelope resulting from the fitted components in bold color; curves are offset for clarity. The \*OH intensity is shaded; its relative intensity varies notably with transition metal. c) Corresponding C 1s spectra, with axis scale taken from b), adjusted to size, and divided by the experimental O 1s:C 1s relative sensitivity factor (RSF). Shown are the CO<sub>3</sub>\* component and adventitious carbon (AC). d) The intensity of the \*H<sub>2</sub>O

peak, outlined in corresponding color in c), scales with that of \*OH. Error bars are defined as the 95% confidence intervals estimated from Monte Carlo simulations.

After a surface was cleaned in O<sub>2</sub> at 300 °C, it remained free of carbon as shown by the C 1s region. The lowest binding energy (BE) is characteristic of oxygen in bulk coordination, while that at ~2.8 eV higher BE was shown by depth profiling (**Figure S3-4**,<sup>23</sup>) to be located at the surface. At intermediate BE ~1.3 eV higher than the bulk, is a feature attributable to \*OH species.<sup>9, 45-46</sup> A carbonate feature became present at higher RH, also at ~2.8 eV above the bulk oxide.<sup>47</sup> The O 1s carbonate contribution was determined from the C 1s integrated area for carbonate, employing an experimentally measured relative sensitivity factor and assuming a 3:1 O:C carbonate stoichiometry (**Figure 2 c**). The intensity of \*OH increased as the sample was cooled to access higher RH, further supporting the peak assignment. At high RH, water adsorbed on the surface, \*H<sub>2</sub>O, with a BE at ~533.3 eV.<sup>9, 45</sup> In addition, the gas phase H<sub>2</sub>O peak is observed at a water partial pressure of 0.1 Torr. Thus by analyzing the evolution of the O 1s and C 1s spectra with RH, the spectra were deconvoluted into different oxygen groups on the surface (**Table S4**).<sup>23</sup>

The perovskite surfaces react with water to form hydroxyl groups, which is evidenced by notable \*OH contribution in the O 1s spectra with increasing RH. The degree of hydroxylation on the perovskite surface is dependent on the transition metal ion: lower intensities of \*OH species on LaMnO<sub>3</sub> and LaCoO<sub>3</sub> than on the other three films are clearly visible in the O 1s spectra, as shown in **Figure 2 b** (**Table S5**). The coverage of \*OH and adsorbed \*H<sub>2</sub>O under the highest RH of the isobar was extracted using a multilayer model proposed recently<sup>23, 48</sup> (**Figure 2 a**, **Table S4, S5**). The \*OH coverage increases in the order of Co < Mn < Ni < Fe < Cr, where a difference up to half a monolayer (ML) reflects significantly different affinities of LaMO<sub>3</sub> toward hydroxylation and binding strengths of \*OH. The coverage of \*OH was also found to scale with adsorbed \*H<sub>2</sub>O, as

shown in **Figure 2 d**, which suggests that water can interact strongly with hydroxyl groups on the surface. Below we discuss how the interactions between water and  $\text{LaMO}_3$  – specifically the coverage of  $\ast\text{OH}$  and  $\ast\text{H}_2\text{O}$  – may influence macroscopic wetting, and ORR activity in basic solution.

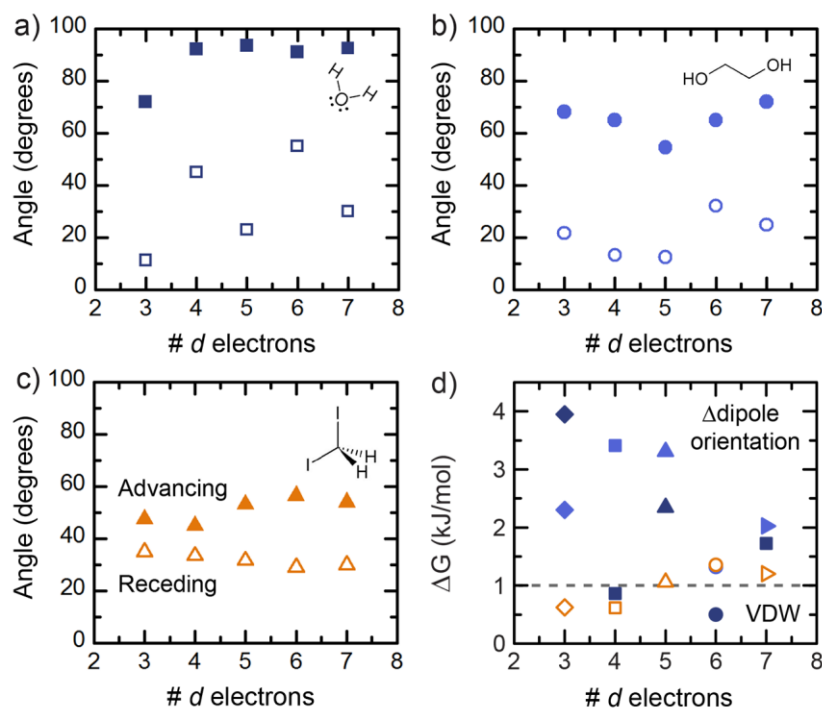
### **Influence of $\ast\text{OH}$ on Macroscopic Wetting**

We first show that the receding contact angle of water in macroscopic wetting trends with the surface coverage of  $\ast\text{OH}$  groups on  $\text{LaMO}_3$  measured by AP-XPS. The macroscopic interaction of  $\text{LaMO}_3$  film surfaces with water was measured by the advancing and receding contact angle. Wetting hysteresis can provide insights into the chemical nature of the water/oxide interface as the contact line experiences different interactions during advancing and receding motion.<sup>49</sup>

All surfaces were moderately hydrophobic in contact with water with advancing angles of  $\sim 90^\circ$ , with the exception of  $\text{LaCrO}_3$   $\sim 70^\circ$  (**Figure 3 a**). We attribute the difference in wettability to the presence of  $\text{Cr}^{6+}$  when exposed to  $\text{O}_2$  gas and its readiness to reduce to  $\text{Cr}^{3+}$  upon wetting (**Figure S6-S7**). This is in contrast to other transition metals in the form of  $\text{LaMO}_3$ , which remain nominally in the 3+ valence state upon exposure to  $\text{O}_2$  gas, and are more resistant to oxidation (**Figure S7**). The higher oxidation state of Cr leads to a more electronegative transition metal center (higher reduction potential), promoting electron transfer upon interaction with  $\text{H}_2\text{O}$  and expected to wet more readily than other  $\text{LaMO}_3$  surfaces, where  $M$  retains the 3+ valence state on the surface. The oxidized  $\text{LaCrO}_3$  surface can also be considered more acidic,<sup>50</sup> which promotes wetting.<sup>51</sup>

In contrast to the advancing angles, the receding contact angles of all  $\text{LaMO}_3$  were notably lower and strongly dependent on the transition metal. Although the difference in the advancing and receding angle is not fully understood at the molecular scale, it is postulated that receding water must break the H-bonds<sup>49</sup> that have formed between surface polar groups and water, thus leading

to stronger interaction with water and a lower receding angle<sup>52</sup> than advancing. To assess this hypothesis, we consider the polar contributions of the oxide surface to dewetting.



**Figure 3.** Advancing (solid) and receding (open) contact angles on LaMO<sub>3</sub> surfaces, with *M* of different *d*-electron number. The probe liquid was a) dipolar water, dark blue, b) monopolar ethylene glycol, medium blue, or c) apolar diiodomethane, orange. d) The free energy of hysteresis,  $\Delta G$ , obtained from the advancing and receding angle of each liquid in corresponding color, is large in magnitude ( $\geq 1$  kJ/mol) for polar solvents, indicative of reorientation of polar surface groups.

For interactions between a solid and a liquid, the change in free energy can be considered as the sum of that arising from apolar Lifshitz-van der Waals ( $\gamma^{LW}$ ) interactions and from polar acid-base interactions. The polar interactions depend on the electron-accepting ( $\gamma^+$ ) and electron-donating ( $\gamma^-$ ) contributions from both surface and probe liquid.<sup>53-55</sup> Thus by measuring the contact angle with three probe liquids of known apolar and polar components and surface tension (**Table S7**), all components of surface energy can be quantified using the van Oss-Chaudhury-Good

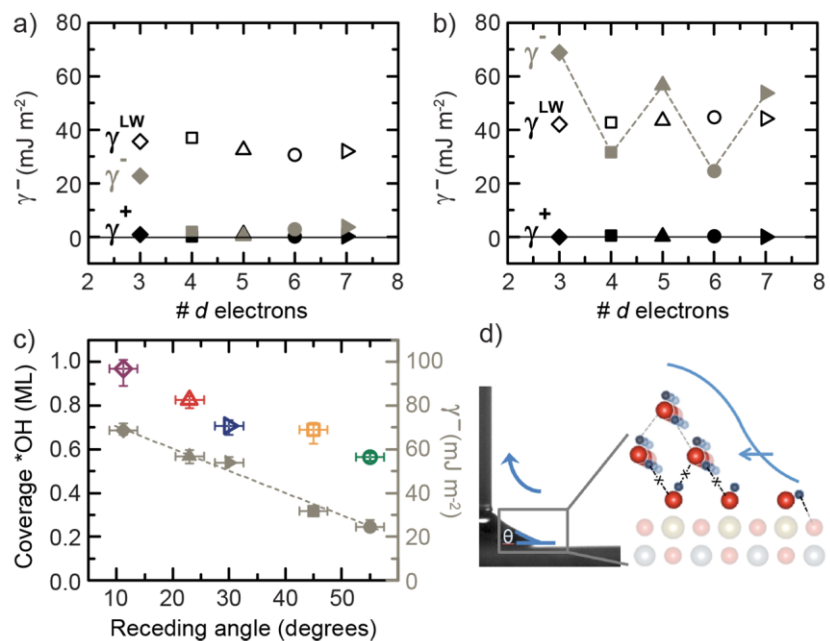
approach.<sup>55-56</sup> The resultant contact angles for each liquid are shown in **Figure 3**. The advancing angle was highest for polar liquids and depended weakly on the transition metal of  $\text{LaMO}_3$  surfaces. In contrast, the receding contact angle varied notably with  $M$  for a polar probe, but remained approximately constant for all surfaces probed with apolar DIM. Notable hysteresis was seen in the contact angle of polar  $\text{H}_2\text{O}$  and EG, in contrast to that of DIM.

The associated free energy of hysteresis in wetting enables a direct experimental comparison of the strength of interaction between the surface and probe liquids of different polar character. The free energy of hysteresis for apolar DIM is  $\sim 1$  kJ/mol and varies little with  $d$ -electron number, while for polar EG and  $\text{H}_2\text{O}$  spans from  $\sim 1$  to 4 kJ/mol (**Figure 3 d**). This range is comparable to that attributed to conformational changes in polar groups<sup>57</sup> and/or strong interactions such as hydrogen bonding.<sup>58</sup> Thus, the large free energy of hysteresis can be attributed to oxygen-containing groups<sup>59</sup> and hydroxyl species.<sup>60</sup> We propose that the large hysteresis observed upon wetting with a polar solvent arises from polar groups at the  $\text{LaMO}_3$  surface. The  $\text{LaMO}_3$  (001) surface itself is polar, with alternating planes of  $\text{LaO}$  (+1 charge) and  $\text{MO}_2$  (-1 charge). In contact with the atmosphere, it may compensate for the net surface dipole through numerous mechanisms – including the adsorption of surface species, surface reconstruction, and charge redistribution.<sup>61-</sup>  
<sup>62</sup> Upon changing the environment from ambient air (or DIM) to that of a polar medium, the surface compensation will change dramatically due to interaction with this dielectric, giving rise to a large free energy of hysteresis. We hypothesize a change in the polarity of the oxide surface upon wetting can be achieved by orientation of polar  $^*\text{OH}$  groups such that electron-rich oxygen interacts with the positive dipole of the water molecule, yielding low receding contact angle.

The  $\gamma^{\text{LW}}$  and  $\gamma^+$  components were roughly constant for all  $\text{LaMO}_3$  surfaces for both advancing (**Figure 4 a**) and receding (**Figure 4 b**) contact angles. In contrast, the  $\gamma^-$  component, roughly zero



for the advancing angle, was found to be much larger and strongly dependent on the transition metal for the receding contact angle, and linearly increases with \*OH coverage (**Figure 4 c**). These observations indicate that strong H-bonding interactions at the oxide/water interface leads to lower receding contact angles (**Figure 4 d**). Although lanthanide-containing perovskites are known to have high affinities for carbonate formation,<sup>63</sup> the correlation of receding angle with \*OH coverage and measurement of surface energy using carbon-containing probe liquids suggests the receding contact angle reflects strong interactions with polar hydroxyl groups on the surface. Both hydroxyl and water coverage (**Figure S8**) and electron-donating polarity (**Figure 4 b**) exhibit a W-shape trend with transition metal *d*-electron number. Inverse W-like trends have been reported among catalytic studies of perovskites such as O<sub>2</sub> adsorption and hydrocarbon oxidation,<sup>64</sup> as well as ORR.<sup>11</sup> Here we propose that the polarity of the water/oxide interface can be influenced by the coverage of polar species on the surface and/or the charge distribution of the surface hydroxyl groups. This hypothesis is supported by the fact that decreasing receding angle correlates with increasing both the electron-donating polar contribution to the oxide surface free energy in dewetting and coverage of \*OH on LaMO<sub>3</sub> measured from AP-XPS (**Figure 4 c**).



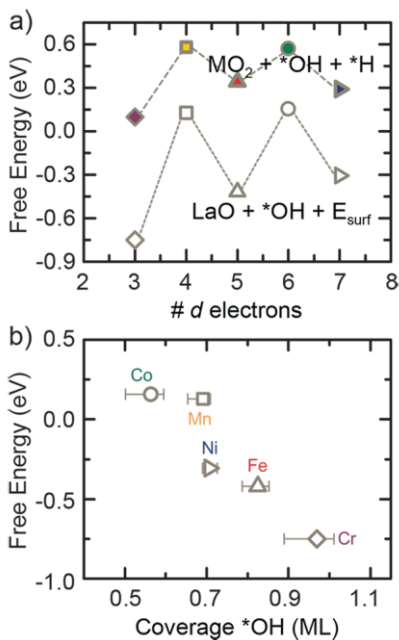
**Figure 4.** Molecular insight into dewetting and contact angle hysteresis. a) The apolar ( $\gamma^{LW}$ ), electron-accepting ( $\gamma^+$ ), and electron-donating component ( $\gamma^-$ ) to the advancing contact angle and b) the receding angle.  $\gamma^{LW}$  and  $\gamma^+$  do not trend with transition metal or exhibit hysteresis, however the electron-donating component ( $\gamma^-$ ) forms a W-shape with  $d$ -electron number for the receding angle. c) The receding contact angle is lowest for the surface with the highest coverage of \*OH (measured in the most humid condition  $\sim 0.3\%$  RH by AP-XPS, error as in **Figure 2**), and reflects H-bonding by electron-donating surface groups,  $\gamma^-$ . Error bars were determined from the spread in calculated  $\gamma^-$  resulting from duplicate measurements on the same film. All dotted lines are to guide the eye. d) Schematic for the receding contact angle, where surface \*OH groups can reorient in the polar liquid medium and interact strongly with water. The need to break H-bonds is indicated with an “X”.

### Assessing \*OH Affinity Theoretically

To further test this hypothesis, we calculated the free energy of adsorption of \*OH and \*H (dissociated water) on LaO and  $MO_2$  terminations by DFT+U calculations (additional details of

the thermodynamic approaches are provided in Supporting Information), corresponding to the reduction of surface energy upon hydroxylation. The stability of the different species on the two surface terminations, assuming the system is in thermodynamic equilibrium, should correspond to their relative abundance. Since the surface stability also depends on the chemical potential of metals in the bulk, such a calculation requires definition of the La and  $M$  chemical potentials. These metal chemical potentials are not independent variables and their sum is fixed by the condition that the system is in equilibrium with bulk  $\text{LaMO}_3$ . We have compared the (001) LaO and  $\text{MO}_2$  surface energy values<sup>65-66</sup> obtained in both the La-rich (system in equilibrium with  $\text{La}_2\text{O}_3$ ) and the  $M$ -rich conditions (system in equilibrium with the  $\text{MO}_x$  binary oxide compounds) (**Figure S9**). These two conditions can be considered as the two metal potential limits where the perovskites are stable with respect to the binary oxide compounds. The relative stability of the various hydroxylated surfaces was assessed by comparing the adsorption energy on the  $\text{MO}_2$  surface to that on the LaO surface adjusted for the difference in surface energy between the facets, both are referenced to the ideal (001)  $\text{MO}_2$ -surface at the 1.20 V vs. SHE (**Figure S10-S11**).

When comparing the adsorption free energy on the two surface terminations, we observe that the LaO surface has a higher affinity for water and hydroxyls groups. To gain insight into more humid environments, we then compute the free energies of the hydroxylated surface: a full monolayer of  $\ast\text{OH}$  and  $\ast\text{OH} + \ast\text{H}$  (dissociated water) on the LaO and  $\text{MO}_2$  surfaces respectively (**Figure 5 a**), both relative to the bare  $\text{MO}_2$  surfaces. These hydroxylated surfaces are expected to better reflect the interactions between adsorbates present on a wetted surface. Both adsorption energies exhibit an inverse W-shape with the number of  $d$  electrons, accounting for the differences in surface energy compared to the bare  $\text{MO}_2$  surface. This trend in the reduction of surface energy upon hydroxylation is reflected in the ease of removing a macroscopic droplet of water.



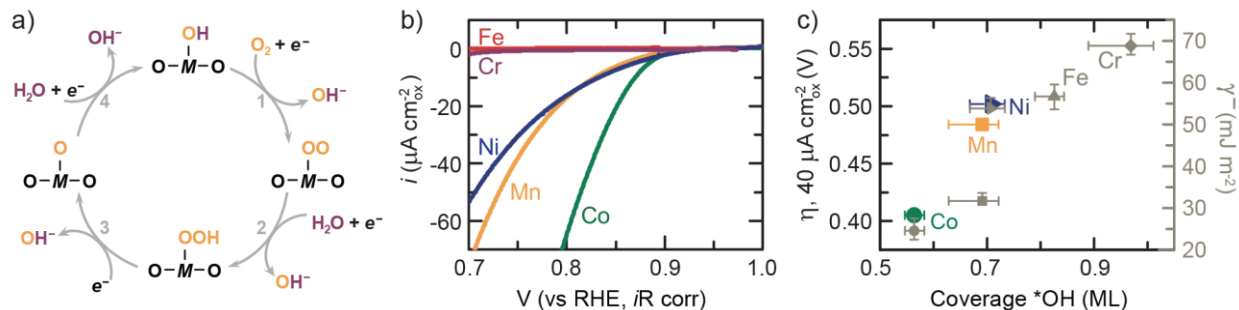
**Figure 5.** Density Functional Theory (DFT) calculations of hydroxylation energetics accounting for the difference in surface energies compared to the bare  $MO_2$  surface at the condition of  $LaMO_3$  in equilibrium with  $La_2O_3$  (**Supporting Information**). a) The DFT-calculated free energies for full coverage of water dissociative adsorption on  $MO_2$  surfaces (filled) and hydroxylation of LaO surfaces (open) show a similar inverse W-shape to the receding contact angle. b) The DFT-calculated free energies for the hydroxylation of LaO surfaces correlates with the coverage measured experimentally by AP-XPS.

The computed surface free energies of the stable hydroxylated LaO termination with 1 monolayer  $*OH$  relative to the bare  $MO_2$  surface trends with the experimental coverage measured at 0.3% RH by AP-XPS (**Figure 5 b**). The correlation suggests the coverage from AP-XPS experimentally assesses the relative affinity of a surface toward hydroxylation. The physical origin to different receding angles therefore resides in the transition-metal-dependent affinities toward hydroxyl formation and electron-donating polarity ( $\gamma^-$ ) on  $LaMO_3$  surfaces.

### Implications of $*OH$ on the Oxygen Reduction Reaction

Looking forward to the potential implications of the interaction between \*OH and H<sub>2</sub>O in designing functional chemistry, we examine these LaMO<sub>3</sub> films for aqueous oxygen electrocatalysis and we report that ORR activity trends inversely with \*OH coverage measured under humid conditions. The interaction between \*OH and water on the LaMO<sub>3</sub> surface can bridge the wetting behavior with their ORR catalytic activity. In basic solution, ORR proceeds on hydroxylated oxide surfaces with a proposed mechanism shown in **Figure 6 a**.<sup>11, 67</sup> O<sub>2</sub> displaces \*OH (step 1), and subsequent reduction leads to a final step, where water re-protonates the surface (step 4), thus the binding and coverage of \*OH can play an important role in the ORR activity.<sup>14</sup>

We measured the intrinsic activity of the (001)-oriented perovskite films toward the ORR (**Figure 6 b, Figure S12**) using methods established recently,<sup>30</sup> where carbon and binder additives used for oxide powder measurements were not needed. The overpotential,  $\eta$ , (kinetic loss) to provide intrinsic ORR current of 40  $\mu\text{A cm}^{-2}_{\text{ox}}$  was found to increase from  $M = \text{Co, Mn}$  to Ni. For the inactive  $M = \text{Fe}$  and Cr, meaningful current densities could not be obtained without potential reduction of the oxide due to the lack of carbon ORR current. Interestingly, the ORR activity trends inversely with the coverage of \*OH measured by AP-XPS, where the most active catalyst LaCoO<sub>3</sub> has the smallest amount of \*OH (**Figure 6 c**). Although the absolute coverage of \*OH depends on pH,<sup>1, 68</sup> this trend of \*OH on LaMO<sub>3</sub> measured in water vapor gauges the relative affinity of these surfaces toward hydroxylation. Greater \*OH coverage, indicative of an increased binding strength of \*OH, can hinder the displacement of \*OH by molecular oxygen (step 1 in **Figure 6 a**), which is considered to be rate-limiting for ORR,<sup>11</sup> and lower ORR activity.



**Figure 6.** Affinity toward hydroxylation describes ORR and wetting. a) Schematic of the mechanism for the oxygen reduction reaction (ORR) proposed by Suntivich et al.<sup>11</sup> and Goodenough et al.,<sup>67</sup> noting the \*OH species between step 4 and 1. b) Capacitance-corrected cyclic voltammetry at 10 mV/s in O<sub>2</sub>-saturated 0.1 M KOH. c) The overpotential ( $\eta$ ) required to achieve a given ORR current, extracted from CVs, correlates with the coverage of \*OH (left axis), where an inactive surface is more hydroxylated, with a higher electron-donating component ( $\gamma^-$ ) to dewetting (right axis, error as in **Figure 4**). ORR activity of LaCrO<sub>3</sub> and LaFeO<sub>3</sub> is too low to obtain meaningful current without potential reduction of the oxide due to the lack of carbon ORR current.

## CONCLUSIONS

In summary, we establish the molecular descriptor of \*OH coverage for both the receding contact angle and ORR activity. Increasing \*OH coverage on perovskites correlates with lower receding contact angle, greater electron-donor character of the surface and lower ORR activity. We show for the first time that the tendency of a polar LaMO<sub>3</sub> surface toward hydroxylation can influence macroscopic wetting properties and oxygen electrocatalysis. We note that extension of these trends to broader classes of surfaces and ranges of hydroxyl affinity requires further investigation, however current understanding suggests that the design of highly active ORR catalysts should consider the intrinsic hydrophobicity of oxide chemistries and their tendency to

hydroxylate. Thus, this study opens a new door to study and exploit hydrogen-bonding on polar surfaces to design functionality at the solid/water interface.

#### ASSOCIATED CONTENT

**Supporting Information.** Further experimental details, additional characterization and measurements, details of calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

##### **Notes**

The authors declare no competing financial interests.

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