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Activity and Stability Trends of Perovskite Oxides for Oxygen Evolution Catalysis at Neutral pH

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Perovskite oxides (ABO_3) have been studied extensively to promote the kinetics of oxygen evolution reaction (OER) in alkaline electrolytes. However, developing highly active catalysts for OER at near-neutral pH is desirable for many photoelectrochemical/electrochemical devices. In this paper, we systematically studied the activity and stability of well-known perovskite oxides for OER at pH 7. Previous activity descriptors established for perovskite oxides at pH 13, such as having an e_g occupancy close to unity or having an O p-band center close to Fermi level, were shown to scale with OER activity at pH 7. Stability was a greater challenge at pH 7 than at pH 13, where two different modes of instability were identified from combined transmission electron microscopy and density functional theory analyses. Perovskites with O p-band close to Fermi level showed leaching of A-site atoms and surface amorphization under all overpotentials examined at pH 7, while those with O p-band far from Fermi level were stable under low OER current/potential but became unstable at high current/potential accompanied by leaching of B-site atoms. Therefore, efforts are needed to enhance the activity and stability of perovskites against A-site or B-site loss if used at neutral pH.

Developing highly active electrocatalysts with fast kinetics for the oxygen evolution reaction (OER) near room temperature is critical to improve the efficiency of many electrochemical technologies in pursuit of sustainable energy, such as water splitting using light or electricity,¹⁻³ and rechargeable metal-air batteries.^{4, 5} Recently, many perovskite transition-metal oxides (ABO_3) have been developed with comparable activities to precious-metal-based catalysts in high-pH alkaline solution with lower cost.⁶⁻¹² In addition, by changing A- and B-site cations, perovskite oxides could also serve as a model system to find the activity and stability descriptors for developing new catalysts. In alkaline electrolyte, the perovskites with an e_g occupancy close to unity⁹ or an O p-band center close to

Fermi level⁸ exhibited the highest specific OER activity. However, as we previously reported, perovskites with an O p-band too close to the Fermi level (> -1.75 eV relative to the Fermi level) such as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-6}$ (BSCF) showed surface amorphization during OER at pH 13 with the surface converting to a layered (hydr)oxide due to A-site loss (i.e. Ba and Sr),^{8, 13, 14} while $PrBaCo_2O_{5+6}$ (PBCO) is just inside the stable region.⁸ At the same time, a systematic investigation of stability and activity of perovskite oxides at neutral pH is still missing; the insights are important for the knowledge-guided design of non-precious-metal oxides catalysts for many electrochemical devices that benefit from neutral or slightly acidic operation conditions, including cocatalysts for photoanodes,^{3, 15, 16} water-oxidation-coupled CO_2 reduction¹⁷ and rechargeable Zn-air batteries¹⁸ to avoid carbonate formation. In this paper, we report the O p-band dependency of activity and stability of perovskite electrocatalysts for OER at pH 7. We identify two origins of corrosion and their effect on longevity and activity of the electrocatalysts, which separates perovskites at pH 7 into two classes, requiring separate strategies for optimization.

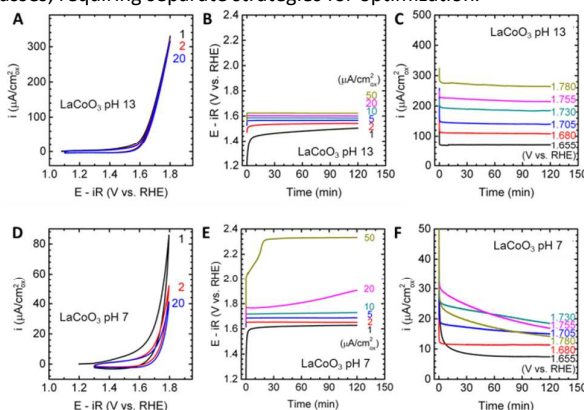


Figure 1. Electrochemical measurements of the $LaCoO_3$ OER activity. (A)(D) Cyclic voltammetry. Numbers indicate cycles. (B)(E) Galvanostatic experiments at various current densities. (C)(F) Potentiostatic experiments at various voltages. (A)-(C) was measured in pH 13 electrolyte prepared with 0.1 M KOH, while (D)-(E) was measured in pH 7 electrolyte prepared with 0.4 M NaH_2PO_4 , 0.6 M Na_2SO_4 and proper amount of NaOH.

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We used micron-sized LaCoO_3 as a starting point to explore the stability window of the perovskites in pH 7 electrolyte prepared with 0.4 M NaH_2PO_4 , 0.6 M Na_2SO_4 and proper amount of NaOH. LaCoO_3 has long been known as a stable and active electrocatalyst in alkaline media,^{9, 10, 19} which we also verify here by cyclic voltammetry (CV; Figure 1A) from 1.1 to 1.8 V vs. reversible hydrogen electrode (RHE), galvanostatic measurements up to $50 \mu\text{A}/\text{cm}^2_{\text{ox}}$ (Figure 1B), and potentiostatic measurements up to 1.78 V vs. RHE (Figure 1C). A clear OER current reduction (i.e. overpotential increase at fixed current or vice versa) was noted from pH 13 (Figures 1A-C) to pH 7 (Figures 1D-F). Moreover, in contrast to stable CV in 0.1 M KOH at pH 13, LaCoO_3 showed a considerable OER current decrease with CV cycling at pH 7 (Figure 1D), which is in good agreement with activity loss above $10 \mu\text{A}/\text{cm}^2_{\text{ox}}$ (Figure 1E) or above 1.7 V vs. RHE (Figure 1F). A similar instability under high OER current/potential at pH 7 can also be found in LaNiO_3 , LaMnO_3 and LaFeO_3 (Figure S1-S3). The origin of this instability will be discussed in detail below.

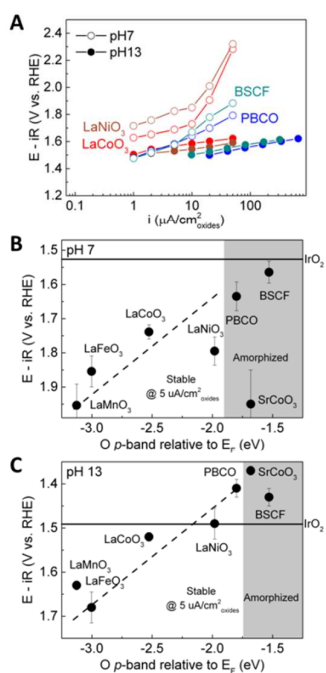


Figure 2. (A) Tafel plots of LaNiO_3 , LaCoO_3 , BSCF and PBCO at pH 7 and 13, obtained from galvanostatic measurements. (B) The p-band center trend at pH 7 of selected oxides at $5 \mu\text{A}/\text{cm}^2_{\text{ox}}$. (C) The p-band center trend at pH 13 at $5 \mu\text{A}/\text{cm}^2_{\text{ox}}$. The horizontal lines in (B) and (C) represent the activity of IrO_2 at $5 \mu\text{A}/\text{cm}^2_{\text{ox}}$. Here O p-band positions were calculated using DFT. All activities were obtained from galvanostatic measurements after 2 hours. The error bars in above figures represent the standard deviation of multiple measurements. Raw activity curves can be found in Figures S5 and S6 in the SI.

All the perovskites examined in this study showed reduced OER activities at pH 7 relative to pH 13 (Figure 2), with comparable Tafel slopes at low overpotentials ($\sim 100 \text{ mV}/\text{dec}$) to those found at pH 13 ($\sim 70 \text{ mV}/\text{dec}$)⁸ but much greater slopes ($\sim 300 \text{ mV}/\text{dec}$) at high

current/potential (Figure 2A). The increased Tafel slope at high current/potential might be related to the loss of A-site or B-site atoms, and these degradation processes will be discussed in detail in a later section. The reduced OER activity at pH 7 might be caused by poisoning of active sites by phosphate. It is interesting to note that commercial IrO_2 had a higher OER activity than all of the perovskites at pH 7 but not at pH 13, maybe due to its high resistance to surface poisoning and extreme chemical stability across a wide pH range.²⁰⁻²³

Here we also examine if OER activity descriptors established for perovskites at pH 13^{8,9} can scale with the activities found at pH 7 (Figure 2A). As none of these perovskites exhibited constant potential responses above $20 \mu\text{A}/\text{cm}^2_{\text{ox}}$ at pH 7 (e.g. Figure 1E), a specific current of $5 \mu\text{A}/\text{cm}^2_{\text{ox}}$ was used to compare the OER activity at pH 7 (Figure 2B) and pH 13 (Figure 2C) as compared to 50 or 500 $\mu\text{A}/\text{cm}^2_{\text{ox}}$ at pH 13 in our previous works.^{8,9} Both OER activities at pH 7 and pH 13 were found to increase with moving the DFT-computed O p-band center closer to the Fermi level. Moreover, the e_g occupancy (taken from our previous study⁹) can serve as an activity descriptor at pH 7 (Figure S4A). These observations suggest that OER activity descriptors previously established for perovskites at pH 13 such as e_g occupancy close to unity⁹ and O p-band center closer to Fermi level⁸ can be extended for the OER activity of perovskites at pH 7.

Perovskites with the O p-band far from Fermi level such as LaCoO_3 and LaNiO_3 were more stable than those closer to the Fermi level such as SrCoO_3 and BSCF. The stability of these perovskites before and after OER at pH 7 was analyzed using transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). TEM and EDS data of LaCoO_3 and PBCO are shown in Figures 3 and 4, respectively. It is worth noting several different trends of the stability between pH 7 and pH 13. Firstly, the amorphization of perovskites (shaded region in Figure 2) after OER shifted to a lower O p-band threshold at pH 7. For example, PBCO remained stable after OER at pH 13 while it became amorphous after OER at pH 7 (Figure 4). Secondly, the perovskites in the stable region (unshaded region in Figures 2B and 2C), like LaCoO_3 , could be stable at $50 \mu\text{A}/\text{cm}^2_{\text{ox}}$ at pH 13⁸ while a ten-fold reduction in the current density was necessary at pH 7 to avoid surface amorphization within operation of 2 hours. When exposed to higher current such as $50 \mu\text{A}/\text{cm}^2_{\text{ox}}$ at pH 7, surface amorphization was clearly visible in LaCoO_3 (Figure 3A), accompanied by the leaching of B-site elements (which is Co in LaCoO_3 shown in Figure 3B). This was also observed in other perovskites with O p-band away from the Fermi level including LaNiO_3 (Figure S7), LaMnO_3 (Figure S8) and LaFeO_3 (Figure S9). Thirdly, the perovskites with the O p-band closer to the Fermi level like PBCO became surface amorphized (Figure 4A), which was associated with loss of A-site elements, i.e. Pr, Ba, La..., (Figure 4B) at current densities as low as $1 \mu\text{A}/\text{cm}^2_{\text{ox}}$. Similar surface changes were also observed after soaking at pH 7 for 2 h without applying any current/potential for PBCO (Figure 4B), BSCF (Figure S10) and SrCoO_3 (Figure S11). In fact, calculated Pourbaix diagrams of perovskites from conditions giving rise to both stable and amorphization perovskites in Figure 2 predict the thermodynamic instability of A-site ions at pH 7 in the OER region (Figures S12-S14), indicative thermodynamic driving force for leaching of A-site ions at lower pH. However, A-site leaching was only observed for oxides

undergoing amorphization. This suggests that the kinetics of A-site leaching and hence amorphization were sluggish for those oxides with O p-bands far from the Fermi level. In previous study at pH 13, the loss of A-site cations led to increased access of the electrolyte to active transition metal sites and thus to an enhancement of the electrochemically active surface area.^{13, 14} In contrast, the oxides with p-band center far from the Fermi level tended to leach more B-site cations such as Co and Ni than A-site La under high current/potential at pH 7, which are proposed as active sites for the OER.^{8, 9} However in this study, due to the potential poisoning effect that has great suppression influence on OER activity at pH 7, it is hard to isolate the consequence of A-site and B-site leaching to the OER activity. It is also worth noting that the stability trends observed in this work are based on rotation-disk electrochemical stability test, which might be different from other stability tests such as scanning flow cell/ inductively coupled plasma mass spectrometry (SFC/ICP-MS)²⁴ and real-device tests.

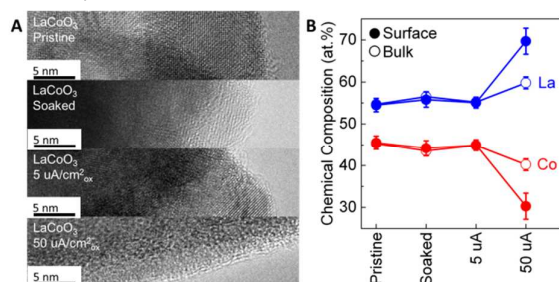


Figure 3. (A) TEM images and (B) EDS-determined chemical compositions of LaCoO₃ in pristine state and operated at 0 (soaking), 5 and 50 $\mu\text{A}/\text{cm}^2_{\text{ox}}$ for 2 h at pH 7. The error bars in (B) represent the standard deviation of multiple spots.

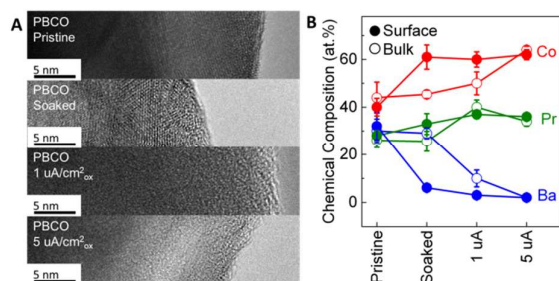
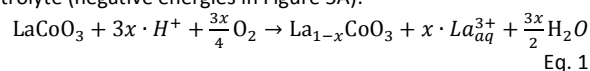


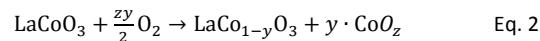
Figure 4. (A) TEM images and (B) EDS-determined chemical compositions of PBCO in pristine state and operated at 0 (soaking), 1 and 5 $\mu\text{A}/\text{cm}^2_{\text{ox}}$ for 2 h at pH 7. The error bars in (B) represent the standard deviation of multiple spots.

For oxides with O p-bands far from the Fermi level, such as LaCoO₃, the consistent lower OER activity at neutral pH vs. pH=13 and the greater surface adsorption energies of the OER intermediates vs. the oxides with higher O p-band²¹ result in a need of much higher over-potential condition at neutral pH to reach the high OER current. Consequently, the high potential/current condition enhances the thermodynamic driving force of the oxidation of B-site ions that is associated with amorphization and thus phase separation (such as a CoO₂ phase, see SI for more details), rather than the leaching of La³⁺, suggesting an oxidation-related degradation process. To test this hypothesis, we performed

density functional theory (DFT) calculations on LaCoO₃ to estimate the thermodynamic driving force of La (A-site) leaching into the electrolyte (negative energies in Figure 5A):



and of Co (B-site) phase separation (negative energies in Figure 5B)



The electrochemical expressions of the above reactions and other DFT details can be found in SI. We selected the potentials of 1.23, 1.75 and 2.33 V vs. RHE to illustrate trends in a range slightly larger than the potentials used in the experimental measurements (Figure 2B). The formation of a Co(IV) phase is justified by the large overpotentials relative to the Co(III)/Co(IV) redox couple at ~ 1.6 V vs. RHE in cobalt (hydr)oxides.^{25, 26} Based on the computational standard hydrogen electrode method^{20, 21, 27} and the assessed stability of the solvated La³⁺, in Figure 5 we showed that both A-site and B-site leaching reactions were energetically favorable to occur at high potential of 2.33 V vs. RHE with reaction energy exhibiting a monotonically downhill trend when the cation vacancy (x or y) increased (-0.8 and -1.4 eV for the reactions in Eq. 1 and 2 at x or $y = 0.5$, respectively). This result supports the B-site leaching and surface amorphization of LaCoO₃ observed by TEM after high current/potential treatment (Figure 3). On the other hand, the thermodynamic driving force for surface changes is very low at this potential considering that the reaction energies of Eq. 1 and 2 were within 0 to -0.3 eV at 1.75 V vs. RHE and an inherent error of the adopted DFT methods was assumed to be ± 0.2 eV per formula unit.²⁸ Moreover, for both A-site and B-site cations, the existence of convex hulls (minimum leaching energy around x or $y = 0.25$) at 1.75 V vs. RHE in Figure 5 indicate the thermodynamic driving forces of cation leaching can be balanced by the repulsion interaction between cation defects at the concentrations around 0.25 (Figure 5). These DFT results are consistent with TEM observations (Figure 3A), where at low current/potential the surface amorphization and B-site loss predicted by Pourbaix diagram were not observed. On the other hand, at the investigated maximal cation vacancy concentration of 0.5, the reaction free energy of Co leaching is -0.6 eV more stable than that of La leaching, suggesting the higher thermodynamic tendency of the Co leaching vs. La leaching near the surface of LaCoO₃ under high potential of 2.33 V, which is in agreement with surface composition of LaCoO₃ from EDS (Figure 3B). Here the enlarged driving force for Co leaching could be from the oxidation of Co into more soluble species at higher potential. Furthermore, previous DFT study²⁹ shown that the missing of less than half B-site atoms on the BO₂ terminations (the stable termination by calculation) can stabilize the layers underneath rather than accelerate the leaching. Therefore the cation point defects at 1.23 and 1.75 V (less than 0.375, see Figure 5) will not cause cation leaching and surface amorphization, in consistent with experimental observations at low potentials. However, at higher potentials, it is noted that the cation vacancy concentration could surpass 0.5 and is likely to lead to point defect-stimulated amorphization.³⁰ Finally, it is conceivable that the catalytic mechanism at pH 7 involves divalent metal cations (e.g. Co²⁺) that can leach into solution where they might be complexed by

phosphate to form insoluble salts such as $\text{Co}_2(\text{PO}_4)_3$. Therefore, it will be critical for the development of more stable electrocatalysts to stabilize the electroactive B-site of oxides with an O p-band away from the Fermi level (e.g. LaCoO_3) against degradation of the active site, especially at higher current densities.

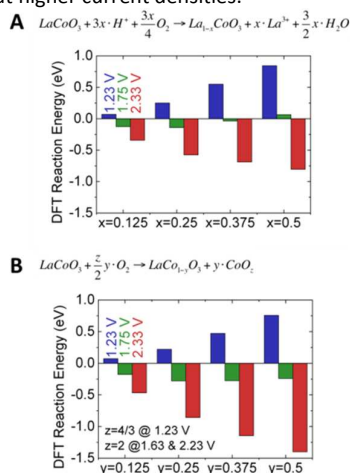


Figure 5. The computed DFT leaching reaction energies of (a) La leaching and (b) Co leaching in LaCoO_3 at various La vacancy concentration (x) and Co vacancy concentration (y), at applied potential of 1.23 V (blue), 1.75 V (red), and 2.33 V (green) vs. RHE at pH 7.

In summary, we systematically studied the activity and stability of perovskite catalysts for OER at pH 7. We found that both an e_g occupancy close to unity or an O p-band close to Fermi level satisfactorily trended with activity at pH 7. New insight was gained into the causes of electrocatalyst instability with the discovery of two different dissolution mechanisms at pH 7. Perovskites with O p-band close to Fermi level showed leaching of A-site cations and surface amorphization at any condition in pH 7 electrolyte, while the perovskites with O p-band far from Fermi level were stable under low current/potential but suffered from phase separation of B-site cations at high current/potential. The joint experimental and DFT modeling results suggest cation leaching due to formation of point defects along with stable corrosion products under applied potentials. Cation leaching plays a more important role for instability at pH 7 as compared to pH 13 because of the much higher OER overpotential under the same current at neutral pH. It is necessary to clearly identify the key material challenges faced in the design of efficient and stable non-precious-metal oxides catalysts for electrochemical devices at neutral pH, such as the A-site vs. B-site instability in different perovskites; optimized design strategies need to be devised to address both challenges separately.

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