Single and double perovskite oxides have been reported to be amongst the most active electrocatalysts for the oxygen evolution reaction (OER) in alkaline electrolyte. Although a detailed study of the bulk electronic structure-activity relationship towards oxygen evolution on these oxides has been reported, the influence of carbon on the behavior of these oxides as OER catalysts is not yet clearly understood. In the present work we study the influence of functionalized acetylene black (ABf) carbon in the electrode composition on the OER activity for perovskite oxides using the thin-film rotating disk electrode technique. It was found that the addition of ABf significantly enhances the OER activity of the single perovskite oxides, namely Ba0.5Sr0.5Co0.8Fe0.2O3, (BSCF) and La0.6Sr0.4Co0.2Fe0.8O3-δ (LSCF). The activity of the double perovskite oxide, Pb0.5Ba0.5CoO3 (PBCO), was relatively unaffected by the addition of ABf in the electrode. Ex situ impedance spectroscopy measurements at room temperature showed that BSCF powder displayed a lower resistivity compared to PBCO with LSCF displaying the highest resistivity of the three materials. These results therefore suggest that the ABf present can more than simply improve the conductive pathway in the perovskite/carbon composite electrodes but can also significantly enhance the electrocatalytic activity of selected perovskites towards the OER.

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The oxygen evolution reaction (OER), the process of generating molecular oxygen through the electrochemical oxidation of water, is a key reaction in energy storage processes involving hydrogen and central to addressing the impending global energy crisis. This reaction, occurring at the anode of the water splitting reaction, is primarily governed by slow kinetics and has therefore been extensively studied to improve the performance of devices such as water electrolyzers. Significant overpotential losses remain a hurdle which requires the need for rare and expensive noble-metal based electrocatalysts for efficient operation. The development and application of new materials able to compete with expensive state-of-the-art current electrocatalysts for hydrogen generating devices therefore yields a great challenge.

Various electrocatalytic materials have been studied in the past towards improving the OER, where the oxides of Ir and Ru have been conventionally identified as the most active, often in mixture with other transition metal oxides. From the numerous metal oxides studied, perovskite oxides emerged as promising electrocatalysts for both the OER and ORR (oxygen reduction reaction) in alkaline media where a number of these oxides have been reported to be sufficiently stable for practical applications. The perovskite-type oxide family, has the general formula ABO3, where the A-site is occupied by an alkaline earth element, such as Ca, Ba and Sr and rare earth elements (lanthanides) such as La or Pr. The B-site is occupied by a transition metal element in 6-fold coordination to the oxygen atoms. The perovskite structure is able to accommodate cation substitution by partial substitution of either the A- or B-site cations with another element yielding a plethora of possible A1-xBxO3 compositions and the potential of tuning the material properties such as catalytic activity, electronic and ionic conductivity, chemical stability and thermal properties. In addition, according to the condition of charge neutrality, electrons/holes or oxygen vacancies at the oxygen lattice sites would be introduced when A- or B-site cations are partially or fully substituted with other cations. As a result, the defect concentration, electrical properties and oxygen mobility are changed, which has led to their use across a broad range of catalytic applications including oxygen electrocatalysis for high and low temperature applications.

Another critical aspect of the perovskite structure is the ability to form ordered structures by stacking of the A- or B-site cations forming layered perovskite structures having a unit cell that is twice the single perovskite crystal structure and are therefore commonly referred to as double perovskite oxides. These oxides usually have the general formula ABO3xB’O3 where the A-site may be occupied by lanthanide and alkali-earth ions and oxygen vacancies are localized into ordered layers.

B0.5Sr0.5CoO3-δ (BSCF) and La0.6Sr0.4Co0.2Fe0.8O3-δ (LSCF) are single perovskite oxides with Co and Fe in different ratios in the B-site and where Ba in BSCF is substituted by La in the A-site to form LSCF. Both have randomly dispersed A-site cations in the crystal lattice throughout the oxide material. PrBaCo2O5+δ (PBCO), is a double perovskite oxide and has alternating Praseodymium (Pr) and Ba ions in the A-site of every crystal lattice forming alternating layers of [PrO3][Co2O4][BaO]O2 as shown in Figure 1. The potential of perovskite oxides for oxygen electrocatalysis was first demonstrated in the late 1970’s by Matsumoto and co-workers. They initially proposed that the formation of a ε” band in the lattice as well as the oxidation state of the transition metal cation (B-site), believed to be the active site, were the main factors determining high OER activity. Bockris and co-workers then showed a relationship between the electronic structure of perovskite oxides and OER activity by looking at the bonding strength of surface oxygenated intermediates as a correlation factor. By studying a number of La1-xAxBO3 perovskites they showed that the oxygen evolution activity increased with decreasing the B-OH bond strength where Ni and Co based perovskites were found to be the most active with LaNiO3 showing the highest OER activity across the 3-d transition metal B-site cations. This finding was explained by the weak bonding strength of the -OH on this perovskite surface.

The development of a more systematic approach to studying the OER and ORR activities of these oxides and the adoption of the thin-film rotating disk electrode (RDE) method conventionally used for noble metal catalysts for studying the OER, a vast number of recent publications have been produced in the study of these materials. With that, further advances have been made in identifying highly active perovskite OER catalysts.

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B-site metal cations. Using this concept as a descriptor they found perovskites with an orbital occupancy close to one, such as LaNiO$_3$ and LaCoO$_3$, to have high OER activity. From the range of perovskite oxides investigated, BSCF showed the highest OER activity, having up to an order of magnitude higher activity in alkaline media than the state-of-the-art IrO$_2$. It has since been shown that BSCF undergoes surface modification under OER conditions, which may ultimately lead to possible altering of the e$_g$ occupancy of the surface Co or Fe atoms in the BSCF perovskite oxide during oxygen evolution to a degree where this correlation may no longer hold.

Double perovskite oxides were then later identified as a family of highly active catalysts for the OER with their activity being attributed to the computed O-p band centre being neither too close nor too far from the Fermi level. Grimaud et al. identified PBCO to have comparable activity to that of BSCF with enhanced stability towards surface modification during the OER measurements in alkaline electrolyte. Furthermore, Raabe et al. looked at a number of Mn-based double perovskites emphasizing the role of oxygen vacancies at the surface of the oxide on the OER activity. While studying the influence of transition metal coordination, the OER activities of cobalt-based perovskites were found to be higher than perovskites containing manganese. This was attributed to the greater flexibility of cobalt ions to adopt several oxidation and spin configurations in the perovskite structure.

Although perovskite materials show promise towards the OER, several of these materials have been found to have rather poor electronic conductivity. Therefore to fully understand their electrochemical behavior using the thin-film RDE method, carbon has often been added to the electrode for thin-film RDE measurements into the considerations that need to be taken into account by the addition of carbon into the electrode for thin-film RDE measurements of perovskite oxide materials for the OER. In this study we evaluate the effect of using functionalized acetylene black carbon (AB$_f$) on the OER activities of Co-based single and double perovskite oxide electrocatalysts for the OER in alkaline electrolyte in composite electrode compositions. We have previously shown enhanced activity of BSCF towards the ORR and OER when AB$_f$ is present and further extend the study to the perovskite oxides LSCF and PBCO using a typical oxide to carbon weight ratio of 5:1. New insights towards the study of these materials with and without the addition of carbon for the OER have been achieved by performing thin-film RDE measurements in alkaline media. This study contributes to a better understanding of perovskite/carbon composite electrodes under OER conditions and provides some important insight into the considerations that need to be taken into account by the addition of carbon into the electrode for thin-film RDE measurements of perovskite oxide materials for the OER.

**Experimental**

**Synthesis of perovskite oxide powders.**—Ba$_0.5$Sr$_0.5$Co$_{1-x}$Fe$_x$O$_{3-δ}$ (BSCF), La$_{0.6}$Sr$_{0.4}$Co$_{1.2}$Fe$_{0.8}$O$_{3-δ}$ (LSCF) and (Pr$_0.5$Ba$_0.5$)CoO$_{3-δ}$ (PBCO) precursor powders were synthesized by a modified sol-gel process as previously described. In brief, stoichiometric quantities of the respective alkali earth and rare earth nitrate precursors and transition metal nitrate precursors (all 99% purity, Aldrich) and Praseodymium(III,IV) oxide (99.9%, Aldrich) were dissolved in an aqueous solution of nitric acid. Citric acid (Aldrich, 99.5%) was added as a chelating agent in a 2:1 ratio with respect to the total metal cations. After obtaining a transparent solution, the pH was carefully adjusted between 6 and 8 by NH$_3$/OH additions. The solution was then heated under stirring to evaporate water until it formed a viscous gel and finally ignited to flame, resulting in a black ash. To obtain single phase oxide material, the BSCF and LSCF powders were calcined at 1000 °C for 2 h in air. PBCO was calcined at 1000 °C for 10 h to ensure single phase material was obtained. The powder was ground with mortar and pestle prior to use.

Acetylene black carbon (denoted AB$_f$, Alfa Aesar) was treated in concentrated nitric acid overnight at 80 °C and then washed and dried prior the utilization. The treatment in concentrated nitric acid has been found to create carbon-oxygen functional groups which improved the reproducibility of the acetylene black activity.

**Characterization of perovskite oxide powders.**—The perovskite structures were confirmed by X-ray diffraction (XRD) analysis. Figure S1 a and b) shows the X-ray diffraction pattern for the single perovskite oxide powders of BSCF and LSCF and c) the double perovskite PBCO oxide powder, to confirm the phase purity of each oxide. The specific surface area of the oxides was determined by Brunauer-Emmett-Teller (BET) analysis. Crystallographic data and the measured specific surface area ($S_{BET}$) data are given in the Supplementary Material S1, Table S1.

**Ex situ impedance spectroscopy.**—To measure the ex situ conductivity for each material, impedance spectroscopy measurements have been performed. The pure oxide electrode powders were kept under a constant pressure of 0.6 MPa for 5 minutes and the electrical resistivity was evaluated by 4-wire impedance spectroscopy measurements at room temperature applying a bias of 100 mV in the frequency range between 1 MHz and 1 Hz. Figure S2 shows typical complex impedance plane plots obtained for pure BSCF, LSCF, and PBCO electrodes from which the conductivity for each oxide was determined. Detailed analysis of the ex situ impedance measurement and the respective electronic conductivity is given in Supplementary Material S2.

**Working electrode preparation.**—For the electrochemical characterization, porous thin-film rotating disk electrodes (RDEs) were prepared from a catalyst ink suspension consisting of 15 mg catalyst, 20 μl Na$_x$-exchanged Nafion solution (Nafion 1100 solution, Alfa Aesar) and 5 ml isopropanol. The catalyst composition comprised of...
either the oxide only or a combination of the perovskite oxide and AB₂ (carbon) or antimony tin oxide (SbSnO₂ 10:90 at%, Nanotek) added in a 5:1 wt. ratio. The catalyst ink was then sonicated for 30 minutes and a known aliquot was drop-coated on a rotating mirror polished glassy carbon electrode (0.196 cm²) and then dried prior to use. All the electrodes presented a ~50 µg cm⁻² Na⁺-exchanged Nafion loading and the same total catalyst loading depending on the oxide used.

**Electrochemical characterization.**—The oxygen evolution reaction (OER) was investigated by thin-film RDE measurements using a home-made Teflon cell with a Biologic VMP-300 potentiostat system. The working electrodes were immersed under potential control (1.0 V vs. RHE) in 0.1 M KOH electrolyte saturated with O₂ at room temperature and the measurements were performed using a hydrogen reference electrode (RHE) separated by a salt bridge with diffusion barrier and a gold counter electrode in a three electrode configuration. The 0.1 M KOH electrolyte was prepared from Milli-Q water and KOH pellets (Sigma Aldrich, 99.99%). Respective cathodic and anodic scans of the disk electrode were performed with a scan rate of 10 mV s⁻¹ at a rotation rate of 1600 rpm. Current densities were normalized by the mass of the perovskite metals (cations) in each of the electrode compositions and all the potentials were corrected for the ohmic-drop measured by electrochemical impedance spectroscopy. Furthermore, to correct for capacitive currents for the OER, an average of the cathodic and anodic scans in O₂-saturated electrolyte was used.

**Electrode loading optimization.**—To account for the respective conductivity values for each oxide powder, the electrode loading for thin-film RDE measurements was optimized for each oxide. Figure S3 shows the current obtained at 1.6 V vs. RHE plotted as a function of the oxide electrode loading, which is an indication of the RDE electrode film thickness for the three oxides studied. Further details on the loading optimization are provided in Supplementary Material S3.

## Results

**Oxygen evolution reaction activity measurements.**—The electrochemical activity towards the OER for pure perovskite oxide electrodes and perovskite/carbon composite electrodes have been evaluated by thin-film rotating disk electrode (RDE) measurements, using cyclic voltammetry at a scan rate of 10 mV s⁻¹ in O₂-saturated 0.1 M KOH electrolyte in the oxygen evolution reaction potential regime (1.0–1.7 V vs. RHE; 1600 rpm). A total of 30 cycles for each electrode composition was performed to evaluate the effect of potential cycling on the OER activity. Table I reports a summary for the activity of the tested electrodes defined as the overpotential at 10 A g⁻¹ metals (average of the anodic and cathodic scans normalized by the amount of oxide metal mass) and the associated Tafel slopes. This normalization method was used given the difficulty in determining the electrochemically active surface area of oxide electrodes using the RDE method and the various limitations reported to be inherent with normalizing for the geometric area, roughness factor or catalyst surface area.

**BSCF and BSCF/AB₂.**—Figure 2a and 2b show the ohmic-drop corrected anodic CV (cyclic voltammetric) scans with a close up for each in the capacitive region given in Figure 2c and 2d for BSCF and BSCF/AB₂ electrodes respectively. It must be noted that the scale on the y-axis differ for these graphs to provide better clarity. Figure 2e and 2f illustrates the capacity- and ohmic-drop-corrected Tafel plots for the BSCF and BSCF/AB₂ electrodes respectively. It can be seen that pure BSCF (i.e. without carbon) does not achieve high OER mass current densities. Small changes in the pseudo-capacitive current region (potential region prior to the onset of oxygen evolution) were observed (Figure 2c) after potential cycling in the OER regime for the pure BSCF electrode. The current density was fairly constant for the 30 cycles performed. It was also noted that the behavior of BSCF catalyst was not fully reproducible and that some samples showed an initial increase in the current density then a decrease while for others small decreases in current density was typically after 20 cycles. The Tafel slope values (see Figure 2e, between ~1.55–1.62 V vs. RHE) were in the range of 82 ± 4 mV dec⁻¹ (initial cycle) and 97 ± 5 mV dec⁻¹ (final cycle), also refer to Table I. The change in the Tafel slope values upon cycling may be a result of some surface modification arising from changes in the oxide surface properties (e.g. morphology, composition, porosity) upon cycling in the OER potential regime. Due to the complexity of the correction of the pseudo-capacitive current and the associated uncertainties thereof, further discussion on the Tafel slope was not carried out. Furthermore a correlation between Tafel slope and oxygen evolution reaction mechanism is out of the scope of the present paper.

The composite BSCF/AB₂ electrode exhibited a different electrochemical behavior compared to the pure BSCF electrode, showing: (i) a higher initial OER current density, (ii) a significant increase in the OER current density upon cycling, and (iii) a fairly constant Tafel slope upon cycling with a value around 68 ± 3 mV dec⁻¹. Furthermore, the increase in the OER current density upon cycling was accompanied by a significant increase in the pseudo-capacitive currents with the formation of a redox peak between 1.3–1.5 V vs. RHE (see Fig. 2d) corresponding to the Co⁹⁵/K⁶⁰ redox couple commonly found for cobalt-based OER catalysts. For pure BSCF electrodes the change in the capacitive current was less significant but a redox peak between 1.3–1.5 V vs. RHE also began to emerge. The surface of BSCF in a BSCF/carbon composite electrode was previously reported to undergo some surface modification upon cycling in the OER region, which was attributed to surface amorphization, which is basically nothing more than loss of crystallinity on the surface due to metal dissolution/re-deposition processes. Our results show a significant increase in current density upon cycling occurring for the BSCF/AB₂ composite electrode while a continuous increase in the current with consecutive cycles was not observed for the pure BSCF electrode material. This observation is also consistent with recently published work showing no increase in the OER activity upon cycling on BSCF-decorated (001)-oriented La₉ₓSr₂₀ₓMnO₃₋ₓ (LSMO) on Nb-doped SrTiO₃ (NSTO) substrates having no carbon present.

**LSCF and LSCF/AB₂.**—Figure 3a and 3b show ohmic-drop corrected anodic CV scans for the OER activity with a close up for each in the capacitive region given in Figure 3c and 3d for LSCF and LSCF/AB₂ electrodes respectively. Figure 3e and 3f show the capacity- and ohmic-drop-corrected Tafel plots for the LSCF oxide and LSCF/AB₂ composite electrodes respectively. The pure LSCF electrode showed a significant decrease in the OER current upon cycling. Tafel slope values varied from ~63 ± 2 mV dec⁻¹ to ~77 ± 2 mV dec⁻¹ for the initial and final cycle respectively. A minimal increase in the capacitive current (see Figure 3c) was also observed.

### Table I. The OER overpotentials at Iₚ = 10 A g⁻¹ metals for the initial and final cycles (30 cycles) for each electrode material.

| Electrode material | Cycle | Overpotential t 10 A g⁻¹ metals | Tafel slope between ~1.55 - 1.62 V vs. RHE (mV dec⁻¹) |
|-------------------|-------|---------------------------------|---------------------------------------------------|
| BSCF              | 1     | Above 470                       | 81.6 ± 4.1                                        |
|                   | 30    | Above 470                       | 96.5 ± 4.6                                        |
| BSCF/AB₂          | 1     | 385 ± 5                         | 67.6 ± 3.4                                        |
|                   | 30    | 315 ± 4                         | 68.7 ± 3.7                                        |
| LSCF              | 1     | 375 ± 5                         | 63.2 ± 1.6                                        |
|                   | 30    | 401 ± 1                         | 77.6 ± 2.4                                        |
| LSCF/AB₂          | 1     | 344 ± 2                         | 74.5 ± 2.1                                        |
|                   | 30    | 359 ± 1                         | 75.4 ± 0.5                                        |
| PBCO              | 1     | 347 ± 7                         | 75.8 ± 4.4                                        |
|                   | 30    | 373 ± 3                         | 81.9 ± 4.1                                        |
| PBCO/AB₂          | 1     | 346 ± 8                         | 82.3 ± 6.2                                        |
|                   | 30    | 381 ± 4                         | 89.2 ± 3.3                                        |
Figure 2. (Color online) Anodic OER currents for the a) BSCF and b) BSCF/ABf (5:1) electrodes measured by at 10 mV s\(^{-1}\) and 1600 rpm in O\(_2\)-saturated 0.1 M KOH. The anodic and cathodic scans of the potential region prior to oxygen evolution is shown for c) BSCF and d) composite BSCF/ABf. Tafel plot for the ohmic and capacitive current corrected (average of anodic and cathodic scans) OER currents at 10 mV s\(^{-1}\) and 1600 rpm for e) BSCF and f) composite electrode BSCF/ABf (5:1).

Discussion

In Figure 5, the mass activity defined as the current density achieved per metal mass loading at 1.57 V vs. RHE for all the tested electrodes in the first and final cycle are summarized. This potential was selected as it was the highest potential at which currents could be compared for all the samples on account of the ohmic-drop correction. It can be noted that the initial mass activity for pure BSCF as for pure BSCF electrodes. In contrast to the BSCF/ABf composite electrode, a decrease in the current for the LSCF/ABf composite electrode was observed upon cycling. The Tafel slope was also similarly unchanged as shown in Table I. The mass activity was higher for the initial cycle of the LSCF/ABf compared to the pure LSCF electrode indicated by a lowering of the overpotential by \(\pm 35\) mV at 10 A g\(^{-1}\) metals, Table I. An increase in the mass activity (±40 mV at 10 A g\(^{-1}\) metals) for the final cycle of the LSCF/ABf electrode compared to the pure LSCF electrode was also observed. This equated to a roughly 3-fold increase in the OER activity of cycling when ABf is present for LSCF compared to the more than 10-fold increase for BSCF when carbon is added to the electrode. Compared to the dramatic increase for the BSCF perovskite oxide with the addition of carbon, these results therefore indicate only a fair interaction between LSCF and ABf occurred as recently described.\(^{38}\)

**PBCO and PBCO/ABf**—Figure 4a and 4b) finally illustrate the ohmic-drop corrected anodic CV scans for the OER activity with a close up for each in the capacitive region given in Figure 4c and 4d for PBCO and PBCO/ABf electrodes, respectively. Figure 4e and 4f) show the capacity- and ohmic-drop-corrected Tafel plots of the pure PBCO electrode and PBCO/ABf composite electrodes in the OER potential regime (1.0–1.7 V vs. RHE). For both the pure PBCO electrode and the PBCO/ABf composite electrode a decrease in the OER current upon potential cycling similar to LSCF and LSCF/ABf can be deduced. In addition, only minor changes in the capacitive currents were observed for both the pure and composite electrodes (see Figure 4c and 4d). Comparing the composite electrode and pure PBCO electrode in terms of OER activity, no enhancement was observed when ABf was present. The Tafel slopes increased only slightly after potential cycling going from \(\sim 75\) ± 4 mV dec\(^{-1}\) to \(\sim 82\) ± 4 mV dec\(^{-1}\) for the pure PBCO electrode and from \(\sim 82\) ± 6 mV dec\(^{-1}\) to \(\sim 89\) ± 3 mV dec\(^{-1}\) for the composite PBCO/ABf electrode.
was significantly lower than that of the pure LSCF while pure PBCO had the highest activity. The higher activity of pure LSCF electrodes compared to BSCF can be ascribed to the higher BET surface area of LSCF compared to that of BSCF (see Table S1, Supplementary Material S1). In addition, changes in the capacitive region are even smaller for LSCF and point to minimal surface modification compared to that of BSCF. It is well known that Ferrite-perovskite cathode materials are generally more stable than Cobaltite-perovskite cathode materials, as observed in high temperature studies where cobalt easily migrates to the surface.39 Therefore, LSCF with lower cobalt content (20 mol %) compared to BSCF (80 mol %) might also present better stability at lower temperatures in alkaline environment. Furthermore, in the LSCF oxide composition, Ba ions are replaced by La and the Sr content in the oxide is reduced compared to that of BSCF. It might therefore be assumed that the presence of La in the lattice structure, coupled with the reduction in Co and Sr ion content stabilizes the lattice of the oxide during OER experiments to a greater extent than for the oxides with higher Co content such as BSCF. However considering the change in the mass activity at 1.57 V vs. RHE upon potential cycling, a decrease of 78% was observed for LSCF while BSCF showed a rather stable mass current upon cycling. Furthermore the layering of the double perovskite structure as for PBCO are also known to better stabilize the Co cations in the structure, preventing major surface modifications in PBCO.40 In fact, no major changes in the capacitive currents were observed for the pure PBCO electrode as well, but as in LSCF a decrease in the mass activity taken at 1.57 V vs. RHE of about 43% occurred upon cycling.

Considering the composite electrodes, the increase in the pseudocapacitive current was not as pronounced for LSCF/ABf and PBCO/ABf compared to BSCF/ABf, suggesting that in the composite electrodes the most significant surface modification occurred for the BSCF/ABf electrodes. The mass activity for the composite electrodes (Fig. 5) did not follow the same trend as for the pure oxide electrodes where only PBCO/ABf showed a negligible change in mass activity compared to pure PBCO. Alternatively, BSCF/ABf showed improved mass activity compared to pure BSCF with a further (and significant) increase in mass activity upon potential cycling. For LSCF/ABf only a relatively small increase in the mass activity was observed compared to the pure LSCF electrodes. These results clearly show that the presence of carbon differently influences the mass activity of perovskite electrodes.
The large increase in current density which translates to an increased OER mass activity, also indicated by a lowering of the overpotential by more than 90 mV to achieve 10 A g\(^{-1}\) metals (Table I) in the composite BSCF/AB\(_f\) electrodes is somehow an unexpected finding. We have observed a decrease in current density for pure functionalized acetylene black carbon upon cycling in the OER regime as shown in Figure 6 and attributed this decrease to an electrochemical oxidation of the carbon, followed by the formation of carbonates in the alkaline electrolyte.\(^3\) Taking this into account and considering carbon degradation upon cycling of the composite BSCF/AB\(_f\)

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**Figure 4.** (Color online) Anodic OER currents for the a) PBCO and b) PBCO/AB\(_f\) (5:1) electrodes measured at 10 mV s\(^{-1}\) and 1600 rpm in O\(_2\)-saturated 0.1 M KOH. The anodic and cathodic scans of the potential region prior to oxygen evolution is shown for c) PBCO and d) composite PBCO/AB\(_f\). Tafel plot for ohmic and capacitive current corrected (average of anodic and cathodic scans) OER currents obtained from a scan at 10 mV s\(^{-1}\) and 1600 rpm for e) PBCO and f) composite electrode PBCO/AB\(_f\) (5:1).

**Figure 5.** (Color online) Mass activity defined as the current (average of anodic and cathodic scans) normalized for the oxide metals loading in the electrode at a potential of 1.57 V vs. RHE for the initial and final cycles (30 cycles) for each electrode material.

Figure 6. (Color online) Anodic OER currents for a pure carbon electrode (AB\(_f\)) between 1.0 and 1.7 V vs. RHE measured at 10 mV s\(^{-1}\) and 1600 rpm in O\(_2\)-saturated 0.1 M KOH, showing the decrease in current density upon cycling.
electrode in this study, the observed increase in the current density of the BSCF/ABf composite electrode appears to be the result of a significant OER mass activity increase when the BSCF catalyst is combined with ABf. Furthermore, we have also observed that when carbon is replaced by another conductive additive, with a low OER activity but higher oxidation stability, such as nano-structured antimony tin oxide powder (SbSnO2), no enhancement in the OER activity was observed (Fig. S4). This indicates some synergetic effect between BSCF and ABf carbon in the BSCF/ABf composite electrode leading to enhanced OER activity. Further studies to investigate the nature of this interaction and the increased activity of BSCF/ABf composite electrodes towards OER are underway. Furthermore, the further increase in OER activity upon cycling points to the existence of a continual process, accelerated by high potential cycling over the number of cycles performed. While it may in fact be as a result of surface amorphization as previously reported further detailed in situ studies are required to fully understand this behavior.

In view of the lower ex situ resistivity of BSCF compared to PBCO and LSCF (See Supplementary Material S2), it is likely that the role of the ABf in the composite cathode is not to simply increase the electronic conduction pathway and increase electrocatalyst utilization. Since BSCF and PBCO show similar order of magnitude resistivity values (62.5 ± 8 kΩ cm for BSCF and 131.3 ± 11 kΩ cm for PBCO, Supplementary Material S2), the ABf addition should equally improve both the BSCF and the PBCO activities. However, this is not the case, as almost no mass activity change was observed for PBCO with ABf carbon addition, suggesting that the addition of carbon in the electrode composition is therefore not required for this oxide as it has no effect on the OER activity. Conversely, the small increase in LSCF activity when mixed with ABf could be still be due to the much higher resistivity of the LSCF oxide material (370 ± 83 MΩ cm, Supplementary Material S2) and therefore even when the oxide loading has been optimized for lower oxide loadings to be used (Supplementary Material S3), conductivity limitations may not be fully overcome for the pure oxide electrode by the addition of carbon.

If one takes into account the different cobalt content of BSCF and LSCF it might be suggested that the large amount of Co in BSCF favors perovskite-carbon interactions responsible for the enhanced activity. However, no carbon influence was observed for the PBCO perovskite which contains even more Co cations in the B-site of the ABO3 structure. Therefore, it appears that the occurrence of a perovskite-carbon interaction, leading to superior performance, is not only dependent on the cations present in the perovskites but also the perovskite structure, i.e. single or double perovskite.

To be able to evaluate the carbon contribution in each of the composite electrode materials the current achieved for each composite electrode was normalized by the mass of the carbon present in each electrode and compared to that of a pure carbon electrode (taken from Fig. 6). Although we are aware that this normalization gives rise to purely virtual activities, it however helps to test the hypothesis of carbon electronically influencing some of the perovskite oxides. It can be seen in Figure 7 that the mass activity per gram of carbon is very low for a pure carbon electrode and therefore contributed only a very small percentage in the composite electrodes (about 5% for PBCO/ABf up to about 10% for LSCF/ABf and BSCF/ABf electrodes) for the initial cycle and even less in the final cycle due to carbon degradation. This indicates that the significant enhancement in the activity when carbon is present cannot be as a result of a contribution from the current observed for carbon degradation, assuming that the oxide does not significantly accelerate carbon oxidation.

Conclusions

The influence of carbon on the oxygen evolution activity of selected single and double perovskite oxides in alkaline electrolyte was described. Thin-film rotating disk electrode analysis was used to show an enhanced OER activity when carbon is present for single perovskite oxides of BSCF and LSCF, while for the layered double perovskite PBCO, no change in the OER activity was observed when carbon was added. The increase in the OER activity for selected perovskites was not found to be correlated to the electrical resistivity of the oxides and points to a synergetic effect between the carbon and the selected perovskite oxides.

Based on this study several important conclusions are drawn. The nature of the interaction between perovskite oxides of different structures and carbon in perovskite/carbon composite electrodes that can lead to improved OER activity needs to be clearly understood in order to further develop better catalytic systems based on perovskite/carbon composite electrodes for the OER. However as a consequence of its significant corrosion at high potentials, the inclusion of carbon may also be detrimental to the performance of such catalyst systems in the long term. One important focus would therefore be to develop alternative electrocatalysts with high OER activity without the need for carbon in the electrode composition. In order to achieve this by improving the rational design of new perovskite oxides for the OER, it is important to understand the intrinsic properties of the perovskite oxides under OER conditions. For this, carbon needs to be excluded from the electrode composition as it may significantly affect the OER behavior of selected perovskite oxides and lead to a misinterpretation of the intrinsic oxide activity.

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