Unconventional Highly Active and Stable Oxygen Reduction Catalysts Informed by Computational Design Strategies

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Discovering and engineering new materials with fast oxygen surface exchange kinetics and robust long-term stability is essential for the large-scale, economically viable commercialization of solid oxide fuel cell (SOFC) technology. The perovskite catalyst material BaFe0.125Co0.725Zr0.75O3 (BFCZ75), predicted to be promising from recent density functional theory (DFT) calculations and unconventional due to its extremely high Zr content and low electronic conductivity, exhibits oxygen reduction reaction surface exchange rates on par with Ba0.5Sr0.5Co0.8Fe0.2O3 (BSCF) and excellent stability at typical operating temperatures. New composite electrodes are engineered by integrating BFCZ75 with commercial electrode materials La1–xSrMnO3 (LSM) and La1–xSrCoFe1–yO3 (LSCF) and achieve high performance as measured by low area specific resistance (ASR) values, with the LSCF/BFCZ75 ASR values comparable to top performing noncomposite electrode materials such as SrCo0.8Sc0.2O3–δ, BaNb0.05Fe0.95O3–δ and BaCo0.6Fe0.22Y0.08O3–δ. The use of BFCZ75 as a composite with LSCF achieving low ASR values shows that BFCZ75 is highly active and can easily integrate into existing SOFC material supply chains, lowering the barrier for potential commercial application of new electrode materials. Finally, these findings point to a broader unexplored class of perovskite materials with high fractions of redox inactive species (e.g., Zr, Nb, and Ta) that may unlock new pathways to realizing improved commercial SOFCs.

1. Introduction

Materials that efficiently exchange and transport oxygen from the environment to the bulk solid-state, sometimes referred to as oxygen-active materials, are an important class of materials for the future of energy technology. These materials function as both conductors of oxygen ions and electrons and are often referred to as mixed ionic-electronic conductors (MIECs). Among the many applications of MIECs, solid oxide fuel cells (SOFCs) receive considerable attention as one of the most efficient, flexible, and clean technologies for the direct conversion of the chemical energy of a fuel into electrical energy.[1–10] The optimal material for an SOFC cathode must satisfy myriad property requirements, such as high electrochemical activity to catalyze the oxygen reduction reaction (ORR), robust stability under operating conditions, high oxygen diffusivity for the efficient transport of oxygen ions through the cathode to the cathode/electrolyte interface, low thermal expansion coefficient (TEC) mismatch between cathode and electrolyte, sufficient electronic conductivity and low overall cost of the cathode raw materials, synthesis, and manufacturing process. During the past few decades, the conventional SOFC cathode design has largely shifted from a composite of electronic and ionic conductors such as La1–xSrMnO3 (LSM)/YSZ to La1–xSrCoFe1–δOδ–δ (LSCF)-based mixed ionic-electronic conductor (MIEC) materials to achieve lower operating temperature and higher power density. During this time, the discovery of numerous perovskite cathode materials (general formula AxA'B1–xO3–δ such as Sm0.5Sr0.5CoO3 (SSC),[11,12] Ba0.5Sr0.5Co0.8Fe0.2O3–δ (BSCF)[13–15] and the double perovskites LnBaCo3O6.5 (Ln = La, Pr, and Gd)[16–19]) have resulted in new MIECs with higher ORR activity than the current commercial materials LSM and LSCF. Despite record-breaking ORR activities, none of these candidate cathode materials have advanced beyond the lab environment to the commercial production line. One key reason for the failure of these materials to be commercialized is due to the issue of material stability, with the limited long-term material stability contributing to the degradation of cell performance, resulting in many current investigations of degradation mitigation methods.[20–23] The operating environment of SOFCs is chemically complex, and operating with ambient air at high temperature often results in the presence of water, CO2, SOx and other species such as CrO3 (released from component interconnects), which can lead to the exsolution of A-site alkaline earth elements (particularly Sr) from the cathode...

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/aenm.202201203.

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DOI: 10.1002/aenm.202201203
matrix to form undesirable secondary phases at the cathode surface and cathode/electrolyte interfaces, severely hampering device performance. For example, the pioneering work of Shao et al. and Shao and Haile demonstrated that BSCF can achieve a high power density of 1010 mW cm$^{-2}$ at a low operating temperature of 600 °C for SOFCs.$^{[13,24]}$ However, under operating conditions, the oxygen permeation flux of BSCF undergoes degradation in a long-term stability test due to the phase transition of the cubic perovskite structure into a hexagonal phase, resulting in a 25% degradation of performance after only 100 h, a clear indication that the material cannot be used for commercial SOFC applications without significant mitigation strategies.$^{[23,25]}$ Even the widely used commercial materials LSM and LSCF react with both the electrolyte and impurities in the air and form performance-degrading secondary phases such as the insulating pyrochlore phase La$_7$Zr$_2$O$_{12}$ at the cathode/electrolyte interface and secondary oxide and hydroxide phases on the cathode surface.$^{[26,27]}$

Critical for the widespread commercial application of SOFCs, cathode materials suitable for use in commercial SOFCs must be robustly stable against materials degradation or reaction with other cell components (e.g., the electrolyte or cell interconnects) and the fuel source (e.g., CO$_2$ in ambient air) for more than 80 000 h at high temperatures (e.g., 700 °C) with a maximum cell degradation rate of 0.3% per 1000 h as indicated by the United States Department of Energy (DOE) Fuel Cell Technologies Office 2020 Technical Targets.$^{[28]}$ To advance SOFC technology and successfully gain more widespread market access, the most urgent task from the standpoint of cathode materials development should therefore be to discover and engineer new materials that are dramatically more stable and with comparable activity to the current commercial cathode materials under the operating conditions of interest, ideally while maintaining or enhancing activity. Cathode materials with improved stability will enable operation at the desired temperature for much longer, reducing operation and material replacement costs, thus improving economic incentives for large-scale adoption of SOFC technology.

Historically, developments of improved perovskite SOFC cathodes have mainly taken the form of individual experimental investigations driven primarily by empirical data and chemical intuition to inform appropriate composition refinement. The general formula of A- and B-site ion substitution to yield $A'_{1-x}B_xO_3$ has been applied to develop new MIEC perovskite materials such as LSCF and BSCF as an advancement over LSM by evaluating the composition space of A, $A'$, and B, with transition metal cations with non-zero d electrons such as Mn, Fe, Co, and Ni.$^{[1–10,29]}$ The key criteria in designing these new MIEC materials like LSCF and BSCF has been focused on high ORR activity and high electronic conductivity. Between these criteria, high electronic conductivity (>100 S cm$^{-1}$) was considered an essential prerequisite for a cathode material and thus restricted the B-site cation element choice to essentially Mn, Fe, Co, and Ni. Based on the studies from the past few decades, the priority given to finding materials with high activity and conductivity has generally resulted in compounds with high activity but poor stability in operating conditions. This conventional strategy to design MIEC cathode materials for SOFCs is flawed, and a new method should be adopted to search for materials beyond the choice of elements historically considered to design materials in this space. However, by broadening the choice of B-site cations and their relative amounts, there are potentially tens of thousands of compositions to evaluate. Screening this new larger space of materials is not practical using conventional experimental approaches, and a computationally based approach may be more efficient.

Recently, first-principles computational modeling using density functional theory (DFT) was successful in informing materials discovery and design of new highly active and stable perovskite SOFC cathodes. DFT-based electronic structure descriptors have enabled the ability to predict values of, and understand trends in, the surface exchange coefficient of perovskite oxide materials, which is correlated with the overall ORR catalytic activity, as well as map out trends in material activity and stability as a function of composition and applied strain.$^{[30–34]}$ Previous work by Jacobs et al. used a sequence of DFT-based screening steps to down-select approximately 50 promising cathode materials for SOFCs from an initial list of more than 2150 perovskite compositions.$^{[33]}$ These approximately 50 promising materials were predicted to have surface exchange rates higher than LSCF, thus indicating predicted improved ORR relative to LSCF, and thermodynamic stability (measured by the energy above the convex hull of the phase diagram formed from the constituent elements) lower than LSCF, thus indicating improved predicted stability relative to LSCF. One of the top candidate materials predicted from this work was BaF$_{0.125}$Co$_{0.125}$Zr$_{0.75}$O$_3$ (BFCZ75), which was found to have high predicted ORR activity (about as active as BSCF) but, unlike materials like BSCF, BFCZ75 was also found to have high predicted thermodynamic stability. While BFCZ75 contains many of the same elements conventionally known to yield high ORR activity, the presence of Zr, in particular its high concentration of 75% on the B-site, provides its high predicted stability. The high amount of Zr makes the high stability of BFCZ75 similar to BaZrO$_3$-based compounds (e.g., Y-doped BaZrO$_3$) extensively studied as proton-conducting electrolytes for proton ceramic fuel cells.$^{[35–38]}$ One would expect that such a high concentration of an inactive element would reduce the concentration of transport mediating vacancies and reactive surface sites, leading to low activity, but, surprisingly, the computations predict high activity. While there have been many recent reports studying the effect of the addition of small amounts of elements such as Zr, Sc, Nb, Tₐ, Y, and Sn to make materials such as SrSc$_{0.125}$Nb$_{0.125}$Co$_{0.75}$O$_3$,$^{[39]}$ BaCo$_{0.6}$Fe$_{0.4}$Sn$_{0.2}$O$_3$,$^{[40]}$ BaFe$_{0.6}$Co$_{0.4}$Zr$_{0.2}$O$_3$,$^{[41]}$ BaCo$_{0.6}$Fe$_{0.4}$Zr$_{0.1}$Y$_{0.1}$O$_3$,$^{[42]}$ and SrCo$_{0.7}$Nb$_{0.1}$O$_{2.3}$,$^{[43]}$ to our knowledge there has only been one report of studying high Zr content, and that study by Sánchez–Ahijón et al. was motivated by the same screening work discussed here.$^{[44]}$ In the work of Sánchez–Ahijón et al., they synthesize BFCZ75 and test its electrochemical performance as an ORR electrode, and find it to have a higher than expected (for a highly active ORR material) ASR of 0.13 Ωcm$^2$ at 800 °C. This level of performance is perhaps not surprising when BFCZ75 makes up the entirety of the electrode (as was the case in Sánchez–Ahijón et al.), as the high Zr content may prompt concerns regarding its ability to function as a highly active material, as noted above. However, we hypothesize the

Adv. Energy Mater. 2022, 12, 2201203 2201203 (2 of 11) © 2022 The Authors. Advanced Energy Materials published by Wiley-VCH GmbH
higher than desired ASR in the work of Sánchez–Ahijón et al. is the result of limited electrical conductivity in BFCZ75, which we solve in the present work by combining BFCZ75 with LSM and LSCF to make high-performing composite electrodes. Further, we find the catalytic materials properties of BFCZ75, including its surface exchange rate, demonstrate it is a highly active ORR material.

In this work, we use experiments, guided by computation, to evaluate the efficacy of the BFCZ family as SOFC cathode materials. In particular, we find that BFCZ75 has both high ORR activity and robust stability at operating temperature. Commercial material LSM- and LSCF-based BFCZ75 composite cell measurements show that the addition of BFCZ75 results in significant activity improvement compared to the use of baseline commercial electrode materials. This work provides a new strategy centered on the inclusion of large fractions of redox inactive species (e.g., Zr, Nb, Ta) to engineer novel perovskite-based SOFC cathodes simultaneously resulting in high activity and high stability and challenging the conventional wisdom of the prerequisites for high-performing SOFC electrode materials.

2. Results and Discussion

2.1. Computational Guidance of BFCZ Stability Trends

A suggestion from the previous work of Jacobs et al., and a key finding we confirm in this work, is that contrary to conventional wisdom and decades of MIEC material design strategy, the inclusion of large amounts of non-transition metal elements in SOFC cathode materials can produce an unconventional, highly active material with improved stability. Since this result is quite surprising, we began our evaluation of the BFCZ system by first determining the expected stability behavior of a broad relevant composition space using density functional theory calculations (see Experimental Section). These calculations serve to broaden the analysis of BFCZ materials beyond BFCZ75 suggested by Jacobs et al.\cite{31} and provide predictive guidance on expected material behavior and trends with transition metal and Zr content. Figure 1 contains a ternary stability map of the BFCZ system with endpoints of BaZrO$_3$, BaCoO$_3$, and BaFeO$_3$. The numbered values correspond to DFT-calculated energies above the convex hull (shown here in units of meV per atom) of the multicomponent phase diagram, where a value of 0 indicates the material is stable (on the convex hull and thus on the phase diagram) and positive values indicate the material is technically unstable but possibly still synthesizable, depending on the magnitude of the instability. As a qualitative guide of relative stability, we have color-coded regions and corresponding material compositions as likely stable (green color, synthesizable and usable in application), likely metastable (yellow color, maybe synthesizable and usable for some period of time in application), and likely unstable (red color, maybe hard to synthesize and possibly useful for a reduced time in application). These stability cutoffs should be viewed as qualitative in nature and are informed based on more detailed studies of DFT-calculated material stability and its relation to observed experimental observations of materials synthesizability and stability.\cite{31,45–47}

From Figure 1, some trends in stability with Fe, Co, and Zr content are directly observable. First, materials with higher Zr content tend to be more stable. Second, the addition of Co results in higher instability (per Co added) than the same addition of Fe, indicating that adding Co generally results in greater instability than the addition of Fe. Moving down the vertical center of Figure 1, which corresponds to different BFCZ compositions with equal amounts of Fe and Co, the stability is greatly increased when progressing from BFCZ25 to BFCZ75, i.e., the predicted stability ranking (most to least stable) is: BFCZ75 > BFCZ50 > BFCZ25. Examination of the predicted activity of these materials based on the work by Jacobs et al. indicates all

Figure 1. Calculated ternary stability map showing trends to DFT-calculated stability, illustrated here as energies above the convex hull in units of meV per atom under typical SOFC operating conditions ($T = 800 \degree C$, $pO_2 = 0.2$ atm). Black dashed lines indicate BFCZ material compositions selected for experimental evaluation in this work. For the composition BaCo$_{0.375}$Fe$_{0.375}$Zr$_{0.25}$O$_3$, the energy above the convex hull value of 76 meV/atom was obtained from averaging over 12 different cation configurations, where the standard deviation of these 12 stability values is 6.8 meV/atom.
three of these BFCZ materials should be highly active (e.g., on par with BSCF), and from the calculations presented here, there should be clearly observable stability trends as a function of Zr content. Thus, we choose BFCZ25, BFCZ50, and BFCZ75 for experimental evaluation of activity and stability, with the aim of choosing the most promising material based on predictions of previous calculations and present experimental observations of sensible tradeoffs between material activity and stability.

2.2. Synthesis and Structure of BFCZ Materials

All BFCZ materials were synthesized from precursor salts using a sol-gel auto-combustion process (see Experimental Section). The X-ray diffraction (XRD) patterns of the high temperature 1250 °C sintered BFCZ25, BFCZ50, and BFCZ75 materials are shown in Figure 2. All of the detected peaks could be indexed to the cubic perovskite structure with no observable impurity phases for all BFCZ compositions. Comparing to the standard BaZrO3 cubic phase, all three BFCZ compositions shift to lower d-spacing with the decrease of Zr content from 75% to 25% by approximately 0.023 Å. As the Zr content decreases, the peak further broadens, suggesting the increase of lattice strain due to oxygen defects and a decrease in crystallinity. We note here that recent work by Sánchez–Alijón et al. on BFCZ75 revealed a trace amount of BaZrO3 with synchrotron XRD. [44] Therefore, the presence of trace amounts of impurity phases such as BaZrO3 in the present BFCZ samples cannot be ruled out.

It is worth pointing out that the synthesis of Zr-doped perovskite (Ba, Sr)(Fe, Co, Zr)O3 has been studied by various groups during the past couple of decades as a strategy to improve the stability of the parent (Ba, Sr)(Fe, Co)O3 material. [23,41,42,48–50] However, the significant formation of stable secondary phases such as BaZrO3 and SrZrO3 has always been observed, impeding the further study of the BFCZ material and potentially suggesting the instability of high Zr content in these materials. For example, Tong and co-workers studied the stability and oxygen permeability of BaCo0.4Fe0.6–δZr0.3O3–δ (x = 0–0.4) and found the cubic perovskite structure was formed for the compositions x = 0–0.2, but phase separation occurred for higher Zr fractions of x = 0.3–0.4. [50] This is one reason research on the BFCZ family has historically focused on Zr content equal to or lower than 20% of the perovskite B-site. The sol-gel combustion synthesis process in this work is a viable synthesis strategy to enable further study of the BFCZ system with high Zr content without secondary phase formation (see Experimental Section and Figure S1 of the Supporting Information).

2.3. Assessing the Activity BFCZ Materials

Having verified we have obtained pure, cubic perovskite BFCZ materials, in this section we turn to evaluate the surface exchange and oxygen diffusivity of BFCZ materials. Figure 3 shows the surface exchange coefficient \( k_{chem} \) as calculated from electrical conductivity relaxation (ECR) measurements (see Experimental Section) as a function of Zr content. We observe \( k_{chem} \) values in the range of 2.67 – 10.4 × 10^{-3} cm s⁻¹ at 750 °C. There are three interesting and important observations that can be drawn from Figure 3 related to the magnitude, range, and trend of the measured BFCZ \( k_{chem} \) values. First, regarding the magnitude, the \( k_{chem} \) values for all BFCZ compositions are high and bracketed by the measured \( k_{chem} \) value of BSCF on the low end (for BFCZ75), and BCFY at the high end (for BFCZ25). BSCF is a well-studied benchmark high activity material, for which all BFCZ compositions investigated here are either on par or surpass the activity of BSCF. In addition, other recent studies of novel very high performing SOFC cathode materials, e.g., SrCo1−βScβO3−δ [51] BaNb0.05Fe0.95O3−δ [52] and BaCo0.6Fe0.22Y0.08O3−δ (BCFY), report log \( k_{chem} \) values at 750 °C of ~2.4, ~2.6 and ~2.0 cm s⁻¹, respectively. Thus, the \( k_{chem} \) values measured here are among the highest ever reported, further illustrating the fact that BFCZ is highly promising from the standpoint of ORR activity. Second, regarding the range in measured \( k_{chem} \), it is striking that changing the Zr content across a wide range results in only a small overall range in measured \( k_{chem} \) values of about 0.6 log units. Third and finally, the data demonstrate that as the Zr content decreases from 75% to 25%, the oxygen surface exchange rate increases. This trend is in qualitative agreement with the previous work of Jacobs et al. and Lee et al., who established trends of the...
surface exchange coefficient $k^o$ (in those studies, measured via isotope exchange depth profiling) with the DFT-calculated O p-band center.\cite{30–32,34} This trend of surface exchange rate with Zr content can also be observed directly from the ECR relaxation curves (see Figure S2 in the Supporting Information). The model fitted kinetic parameters, chemical diffusion coefficient $D_{chem}$ and $k_{chem}$, are summarized in Table 1.

The $D_{chem}$ values for BFCZ compositions studied here tend to be lower than other novel electrode materials recently reported. This is both not surprising and not a concern for our present SOFC electrode design. We believe the lower $D_{chem}$ is the result of the generally higher fraction of redox-inactive species (here, Zr) compared to the other highly active electrode materials. This high Zr content results in fewer oxygen vacancies, thus reducing the oxygen ion diffusivity, which operates by a vacancy-mediated diffusion mechanism. The somewhat lower $D_{chem}$ but high $k_{chem}$ values of BFCZ make these materials prime candidates for engineering composite electrodes with commercial materials like LSCF, which will be discussed in more detail below.

### 2.4. Assessing the Stability BFCZ Materials

To evaluate the impact of the Zr content on the stability of the BFCZ materials and confirm the predicted trend from the computational model, bulk BFCZ25, BFCZ50, and BFCZ75 samples were aged in 20% dry O$_2$ balanced with N$_2$ at 750 °C for 360 hours. ECR tests were carried out every 30 h to monitor the degradation of the surface exchange kinetics. To minimize the impact of the fitting method, the ECR data were analyzed based on the fact that all three bulk phases are stable under the aging condition and no decomposition occurs, which is confirmed by the post-aging XRD characterization (see Figure S3 of the Supporting Information). Hence, the $D_{chem}$ was considered as a fixed parameter based on the zero-hour result during the fitting process. In addition, due to the fast response of BFCZ25 and the system sampling limitation (200 mS), which leads to large fitting error, the ECR tests of BFCZ25 were carried out at 550 °C in intervals of 30 hours aging at 750 °C. As shown in Figure 4, the stability tests show time dependence of the oxygen surface exchange coefficient and the results agree very well with the model prediction on the qualitative stability order of the BFCZ phases: BFCZ75 (most stable) > BFCZ50 > BFCZ25 (least stable). Within the intermediate temperature regime of 600–800 °C in SOFC systems, the commonly used MIEGs such as LSCF experience a significant drop in the ORR kinetics due to surface chemistry change such as Sr segregation.\cite{59,60} Although the factors governing the surface degradation of MIECs remains under active investigation, there have been reports showing that less reducible cations on the surface such as HF$^+$, Ti$^{4+}$, Zr$^{4+}$, Nb$^{5+}$ or Al$^{3+}$, improve the oxygen exchange kinetics and stability of MIEGs such as La$_{0.6}$Sr$_{0.4}$CoO$_3$.\cite{61} The detailed mechanism of the surface degradation of BFCZ phases and its correlation with the oxygen exchange kinetics remains unclear and requires extensive further studies. Here we have demonstrated, both computationally and experimentally, that the amount of Zr$^{4+}$ in the bulk BFCZ system has a strong correlation with the activity and stability. We note that if these fractional losses in $k_{chem}$ were to occur for data taken at the same temperature, then the performance for BFCZ75 would surpass that of BFCZ50 and BFCZ25 at 60 and 90 h, respectively. This demonstrates the value of increasing stability as opposed to just trying to optimize activity.

### 2.5. Stability of the BFCZ/Samaria-Doped Ceria (SDC) Composite

As-made BFCZ25, BFCZ50, and BFCZ75 powders were mixed with an equal weight of SDC powder and sintered at 1100 °C.

![Figure 4. Normalized oxygen surface exchange coefficient $k_{chem}$ aging behavior of BFCZ25, BFCZ50, and BFCZ75 in 20% dry O$_2$ balanced with N$_2$ at 750 °C for 360 h.](Image)
in air for 20 h. Then, the three mixtures were analyzed using XRD to identify potential reactions between the components. As shown in Figure 5, BFCZ75 shows a clean XRD pattern with no signs of reaction with SDC. BFCZ50, on the other hand, clearly shows a broadened shoulder next to the (011) peak, indicating the formation of secondary phase(s). As for BFCZ25, the reaction with SDC is much more extensive and the original BFCZ25 phase has completely disappeared. The newly formed phases show well-defined diffraction patterns (indicated as *). The complete XRD patterns and possible candidates with similar crystal structure were identified (see Figure S4 of the Supporting Information). As we are interested in the stability of the material, not its decomposition products, we have not determined their detailed chemistry and structure at this time due to the complexity of the involvement of six different cations. This result further confirms the prediction of DFT stability calculations and serves as a promising demonstration of using BFCZ75 as an active component to produce an SDC-based or GDC-based composite cathode for SOFCs, as BFCZ75 does not appreciably react with the ceria present in SDC and GDC.

As discussed in the introduction of this work, we believe the most crucial aspect of realizing more widespread adoption of SOFC technology is to focus catalyst discovery and design on finding the most stable materials while high ORR activity is a necessary, but not sufficient, requirement. In light of the previous computational results indicating BFCZ75 is a promising SOFC material and the experimental evaluation of BFCZ materials properties shown here, for the remainder of this study we focus our efforts on further evaluating BFCZ75 as a SOFC cathode material. While BFCZ75 has slightly lower $k_{\text{chem}}$ than its more Zr-poor variants, the robust stability over time at high temperature supports BFCZ75 as more promising for commercial SOFC application compared to the other BFCZ compositions studied here.

2.6. LSM/BFCZ75 Composite Electrode Design and Electrochemical Properties

As an efficient cathode for SOFCs, the material needs to mainly fulfill three roles: 1) high electrical conductivity to complete the circuit and minimize electronic ohmic resistance; 2) high oxygen exchange activity to support rapid ORR kinetics and minimize the polarization resistance; 3) high ionic conductivity to transport the reduced oxygen ion to the electrolyte to minimize the ionic ohmic resistance. State-of-the-art cathodes generally use a composite design to achieve the highest efficiency by mixing highly conductive MIECs such as LSCF (to function as an electronic conductor and active ORR catalyst) and an ionic conductor such as SDC (to transport the oxygen ions). As discussed in the introduction, the requirement of high electronic conductivity (>100 S cm$^{-1}$) has historically limited the search space of new electrode materials to those that must function as MIECs, and this limitation has not thus far been successful in overcoming the critical issue of long-term operational stability. Here, we propose a new type of composite electrode composed of 1) an electronic conductor and 2) a highly active and stable material like BFCZ75 with low electrical conductivity (~0.16 S cm$^{-1}$ at 750 °C, see Figure S5 of the Supporting Information), as an alternate strategy in cathode design. As a proof of concept, we have fabricated two types of composite electrodes by using a 1:1 mass ratio mixture of commercial LSM and LSCF with BFCZ75 in a two-electrode configuration as symmetrical half cells using GDC as the electrolyte. The chemical compatibility was evaluated by XRD after sintering LSM/BFCZ75 and LSCF/BFCZ75 mixed powder at 1100 °C and then aging at 750 °C for 5 days (see Figure S6 of the Supporting Information). The cells were characterized by electrochemical impedance spectroscopy (EIS) at different temperatures in 20% oxygen balanced with nitrogen. As a direct comparison, we also fabricated a pure LSCF electrode, pure LSM, and an LSM/YSZ composite electrode, which were evaluated under the same conditions.

The electrode performance of LSM/BFCZ75 and LSM/YSZ composite electrodes were characterized by EIS from 700 to 850 °C. The pure LSM electrode was fabricated and tested under the same condition as a baseline for comparison (see Figure S7 of the SI). LSM is an electrically conductive oxide with little ionic conductivity and when used alone as the cathode, the polarization resistance is very high. The traditional approach is to use LSM together with YSZ and take advantage of the triple-phase boundary reaction mechanism to accelerate the ORR reaction, with a reduction in polarization resistance by up to 90% (see Figure S7 of the Supporting Information). Here, we show that the performance of LSM/YSZ can be drastically improved by instead mixing LSM with BFCZ75. As shown in Figure 6a, at 800 °C the area specific resistance (ASR) of LSM/BFCZ75 (ASR = 0.74 Ω cm$^2$) electrode is nearly 80% lower than LSM/YSZ (ASR = 3.49 Ω cm$^2$), a nearly 5x reduction in ASR. The ORR mechanism for LSM/YSZ is dominated by triple phase boundaries. By replacing YSZ with BFCZ75, which has greater electrical conductivity than YSZ, the ORR reaction is expected to switch to a different pathway. In the Bode plot of the impedance spectrum shown in Figure 6b, the characteristic frequency of the response shifted from ~1Hz, which is the Bode plot feature corresponding to the ORR mechanism at the LSM/YSZ triple phase boundary, to above 10 kHz for the LSM/BFCZ75 composite. This result suggests the overall ORR rate is significantly accelerated when YSZ is replaced by BFCZ75. For the LSM/YSZ electrode, the dominant impedance
feature around 1 Hz is generally attributed to the dissociative adsorption of oxygen on the surface of the cathode, transfer of oxygen intermediates at the triple phase boundary, and surface diffusion of oxygen. On the other hand, the high-frequency response centered around 10 kHz is attributed to the flow of oxygen ion/intermediates through the YSZ or LSM/electrolyte interface.\textsuperscript{[62]} In the case of LSM/BFCZ75, if we adopt a similar interpretation to that for the LSM/YSZ system, the dominant high-frequency response is from the oxygen ion diffusion in BFCZ75 or the BFCZ75/GDC interface. This high impedance from charge transfer process indicates nonideal microstructure due to the sintering process/condition. Further study of the sintering behavior of BFCZ75 with various electrode/electrolyte materials is needed to address this issue more thoroughly. The low-frequency response around 1 Hz with a magnitude of 0.02–0.03 \( \Omega \text{cm}^2 \) is attributed to the gas phase diffusion process from the porous electrode structure and the porous Pt current collector layer. The middle section of the spectrum is from the ORR process, and, due to the fast rate, it was convoluted with the high-frequency interface process and difficult to identify from the Bode plot. To extract the ORR response from the EIS data, a distribution of relaxation times (DRT) analysis was carried out to aid the interpretation of the spectrum. As shown in Figure S8 in Supporting Information, the deconvolution of the impedance spectrum from 800 and 850 °C shows three main peaks around the relaxation frequencies of \( \approx 3 \) Hz, 1kHz and 25kHz, corresponding to the gas diffusion, ORR and electrode/electrolyte interface process, respectively. The presence of BFCZ75 significantly accelerates the ORR and results in the interface process being the main contributor to the overall polarization resistance as the oxygen diffusion coefficient of BFCZ75 is several orders lower than that of the YSZ. For practical application, the electrode/electrolyte interface could be further engineered such as by adding an ionic conducting backbone (e.g., SDC) to further lower the overall polarization resistance.

As part of the overall loss in SOFCs, the ohmic resistance is mostly attributed to the electrolyte. Due to the low electrical conductivity of BFCZ75, it is important to assess if the ohmic resistance was impacted. Three cells with LSM/SDC, LSM/BFCZ75, and pure BFCZ75 electrodes were fabricated on identical GDC substrates and tested by EIS at 800 °C. As shown in Figure S9 in the Supporting Information, the LSM/BFCZ75 composite electrode shows little impact to the ohmic resistance compared to the LSM/SDC electrode, suggesting that LSM is providing enough electronic conductivity to support the electrode function. However, the pure BFCZ75 electrode, despite its low polarization resistance, shows more than four times higher ohmic resistance value compared to the LSM/BFCZ75 composite. This result indicates that even with high ORR activity, BFCZ75 is not suitable to use as standalone cathode material.

2.7. LSCF/BFCZ75 Composite Electrode Design and Electrochemical Properties

The most active major commercial cathode material, LSCF, was also used to form a composite electrode with BFCZ75. Figure 7a shows the Cole-Cole plot and Figure 7b shows the Bode plot of the LSCF/BFCZ75 composite electrode with a pure LSCF electrode as a comparison. The impedance spectra show two distinguishing features. The low-frequency arc originates from the gas diffusion process of the paste-free Pt current collector layer and remains constant between different samples and therefore can be easily removed by using a standard R–C circuit during the fitting process. The high-frequency arc is attributed to the ORR activation polarization and was fitted by using a R–CPE circuit. The activation energy of both electrodes was calculated from the Arrhenius plot shown in Figure 7c and are very close to each other with a value of about 1 eV, suggesting a similar ORR mechanism for both materials.

In Figure 7(c), the activation polarization ASR of pure LSCF is 0.041 \( \Omega \text{cm}^2 \) at 800 °C. With the addition of BFCZ75, the polarization ASR is reduced to 0.016 \( \Omega \text{cm}^2 \). This ASR reduction of about a factor of 3\( x \) suggests a significantly enhanced ORR rate and is among the lowest reported in the literature. For example, a handful of other recently investigated materials such as \( \text{SrCo}_{0.8}\text{Sc}_{0.2}\text{O}_{3-\delta} \), \( \text{BaNb}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta} \), \( \text{SrCo}_{0.8}\text{Nb}_{0.2}\text{O}_{3-\delta} \), \( \text{BaCo}_{0.6}\text{Fe}_{0.3}\text{Sn}_{0.1}\text{O}_{3-\delta} \) and \( \text{BaFe}_{0.4}\text{Co}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta} \) found log ASR values at 800 °C of \(-2.3, -1.6, -2.0, -2.4 \) and \(-1.7 \) \( \Omega \text{cm}^2 \), respectively, compared to log ASR of \(-1.8 \) \( \Omega \text{cm}^2 \) for the LSCF-BFCZ75 composite reported here. Given the slightly higher measured \( k_{\text{chem}} \) values of BFCZ25 and BFCZ50, it may be possible to obtain even lower ASR values from composite electrodes of these materials, though these electrodes should be expected to have reduced stability. Finally, we note here that in recent work, Sánchez-Ahijón et al. investigated the structural and electrochemical properties of BFCZ75 half cells. The ASR...
of their BFCZ75 half cells measured at 800 °C was 0.13 Ω cm².[44] This ASR value is about 9× higher than the ASR of the LSCF-BFCZ75 composite electrode investigated here. We speculate that this higher ASR value obtained by using pure BFCZ75 as the cathode material is a result of the low electronic conductivity of this material. The dramatic enhancement of the ASR when BFCZ75 is paired with LSCF may therefore be the result of maximizing the individual benefits of BFCZ75 and LSCF, i.e., BFCZ75 performs the ORR rapidly and transports O ions quickly, and LSCF provides the necessary electronic and ionic conductivity so that charge transfer processes do not reduce the overall cell efficiency by increasing its resistance.

2.8. Thermal Stability of BFCZ Composite Electrodes

To investigate the LSM-BFCZ75 and LSCF-BFCZ75 composite electrode stability more thoroughly, we tested the polarization resistance change of LSM- and LSCF-based electrodes under open circuit voltage (OCV) conditions at 750 °C in air for 50 h. The impedance spectra were collected every four hours and the results are summarized in Figure 8. LSM is known to be a relatively stable material, and as shown here the aging behavior is very close between the LSM-YSZ and LSM-BFCZ75 composite electrodes. On the other hand, the LSCF-BFCZ75 composite electrode showed significantly less performance degradation compared to LSCF (by ≈65%), suggesting that BFCZ75 is the active component of the electrode and significantly improves the stability of the performance. It is important to note that these degradation rates are much faster than commercial electrodes. This discrepancy in degradation rates is not surprising and likely due to a combination of quite large differences in the synthesis, processing, and testing conditions for the present materials versus commercial cell degradation assessment. However, the latter is a very large undertaking and outside the scope of the present work. The increased stability observed in this test is encouraging and consistent with generally increased stabilization provided by the BFCZ material, so we have reported it here. However, significantly more testing would be required to determine if degradation effects occur under commercial synthesis, processing, and testing conditions. This analysis thus shows a proof-of-concept of using BFCZ75 as a composite electrode to create high activity, improved stability electrodes compared to presently used commercial materials LSM and LSCF. We believe the performance of BFCZ75 composite electrodes could be further improved, and the optimization of a composite electrode with the inclusion of BFCZ75 presents engineering challenges deserving of further study.

3. Conclusion

In this contribution, we used experiments, guided by computational models, to evaluate the efficacy of BFCZ75 as an SOFC cathode material. We mapped out and provided an understanding of trends in stability and activity (via surface

![Figure 7. a,b) Impedance spectra of LSCF/BFCZ75 and LSCF electrode at 750 °C and 20% O₂ c) Arrhenius plot of the high-frequency section ASR of LSCF/BFCZ75 and pure LSCF electrode.](image)

![Figure 8. Aging behavior of a) LSM- and b) LSCF-based composite electrodes with BFCZ75 under OCV condition at 750 °C in air.](image)
exchange rates) for three compositions in the perovskite Ba-Co-Zr system, and experimentally showed that BFCZ75 has the highest stability at elevated temperatures over prolonged time periods. Remarkably, despite its very high Zr content, we experimentally find that BFCZ75 is still a highly active ORR catalyst material, with a measured surface exchange rate on par with BSCF, while the surface exchange rate of BFCZ25 is among the highest ever reported. Having confirmed the promising intrinsic materials properties of BFCZ25 relevant for SOFC applications, we then fabricated and tested two types of composite electrodes using commercial LSM and LSCF materials. The LSCF-BFCZ75 composite electrode, in particular, showed significant improvement compared to the LSCF baseline material, with a very low log ASR value of $1.8 \, \Omega \cdot \text{cm}^2$ at 800 °C. Considering this result was obtained with simple mixing of commercial LSM/LSCF and as-made BFCZ75 using standard processing methods, the performance of the electrode could be even further improved by optimizing the composition and microstructure.

As conventional strategies of engineering new MIEC materials for SOFCs over the past few decades would have eliminated a material like BFCZ75 from contention, this work suggests there is a need to re-think existing design criteria and develop and understand new rational materials design strategies that challenge conventional wisdom and chemical intuition. The ultimate goal of cathode design of SOFCs is to achieve a balance among electrical conductivity, ionic conductivity, oxygen exchange activity and long-term stability. Instead of searching for a replacement for unstable MIEC like LSCF, which works well in a composite electrode with ceria based ionic conductor, some stable composites contain a highly conductive material mixed with a less conductive but highly ORR active and stable MIEC such as BFCZ75 or even triple-phase composites could be an alternative way to advance the current SOFC technology. This study successfully demonstrates that modern computational-based materials discovery methods can point to unconventional and novel design strategies which would have been either inaccessible to experimental techniques (e.g., too many compositions to examine) or ill-advised based on conventional wisdom (e.g., having too low electronic conductivity by virtue of low transition metal content). These novel design strategies can unlock new high-performing SOFC electrode materials with performance rivaling other state-of-the-art novel cathode materials, while also having improved operational stability and utilizing current commercial cathode material production lines, offering a promising path toward the widespread adoption of SOFC energy technology.

4. Experimental Section

Powder Synthesis and Characterization: Ba$_2$Fe$_3$Ti$_2$O$_{12}$ (BFCZ25), Ba$_2$Fe$_3$Ti$_2$Zr$_{0.5}$O$_{12}$ (BFCZ50) and Ba$_2$Fe$_3$Ti$_2$Zr$_{0.75}$O$_{12}$ (BFCZ75) powders were prepared by a sol-gel auto-combustion process using citric acid as a chelating agent and nitrate ammonium as an oxidant. Stoichiometric amounts of precursor salts Ba$_2$(C$_2$H$_3$O$_2$)$_2$ (Sigma-Aldrich, 99%), Fe(NO$_3$)$_3$·9H$_2$O (Sigma-Aldrich, 98%), Co(NO$_3$)$_2$·6H$_2$O (Sigma-Aldrich, 99%) and ZrO(NO$_3$)$_2$·6H$_2$O (Sigma-Aldrich, 99%) were dissolved in diluted nitric and citric acid solution at 70 °C. The resulting gel was then heated up to 300 °C for 3 h in a muffle furnace followed by a 3 h calcination at 900 °C. The resulting powder was hand ground and pressed into a pellet and sintered at 1100 °C for 5 h to produce the final product. The phase purity and structure of the synthesized materials were analyzed by X-ray diffraction (Philips Panalytical XRD) with Cu Kα radiation (1.514 Å) at room temperature.

Pellet Preparation and Characterization: To prepare the dense bar sample for electrical conductivity relaxation (ECR) experiments, the as-synthesized powder was roller ball-milled in isopropanol for 24 h and then dried at 80 °C. Cylindrical pellets were produced by pressing 0.5 g of BFCZ75 powder with a hydraulic press and sintered at 1200 °C for 6 h. The high density of about >96% was confirmed using the Archimedes method at room temperature. The phase purity was confirmed with X-ray diffraction. Both faces of the as-sintered pellet were polished to remove any surface products formed during sintering and then heated up to 1000 °C for 1 h to form a natural, relaxed surface.

Electrical Property Characterization and Electrochemical Analysis: The electrical conductivity of BFCZ was measured by 4-probe method using Keithley 2200 power source and Keithley 2182A nanovoltmeter. For electrical conductivity relaxation (ECR) measurements, the PO$_2$ change was accomplished using a 4-way-valve to abruptly switch the flowing gas. PO$_2$ range of diluted gas was controlled by mass flow controllers (Alicat) in the range of 0.2 atm to $6.25 \times 10^{-1}$ atm and measured using O$_2$ sensor (Illinois Instruments, Series 800, USA). For MIECs, it is generally assumed that any local change of oxygen vacancy concentration is linearly related to the accompanying electron-hole concentration change. Based on a linearized relation between conductivity and oxygen concentration, the measured electrical conductivity is normalized and is fitted to a 3-dimensional diffusion equation:

$$\sigma_n = \frac{\sigma_1 - \sigma_0}{\sigma_1^0 - \sigma_0^0}$$

$$(1)$$

$$\sigma_n = 1 - \frac{1}{4} \sum_{n=1}^{N} \sum_{n=1}^{N} \sum_{n=1}^{N} 2L_i^2 \frac{\exp(-\frac{B_i^2D_{chem}t}{x^2})}{x^2} \times 2L_j^2 \frac{\exp(-\frac{B_j^2D_{chem}t}{y^2})}{y^2} \times \frac{\exp(-\frac{\phi^2D_{chem}t}{z^2})}{z^2} \times \frac{\phi_p (\phi_p^2 + L_p^2 + L_p)}{L_p^2}$$

$$(2)$$

$$L_j = \frac{x}{D_{chem}}; L_p = \frac{y}{D_{chem}}; L_p = \frac{z}{D_{chem}}$$

$$\beta_m \tan \beta_m = L_j \gamma_\gamma \tan \gamma_\gamma; \gamma_\gamma = L_j \gamma_\gamma \tan \gamma_\gamma$$

$$(3)$$

$$(4)$$

where $\sigma_1$ is the normalized conductivity, $\sigma_1^0$ is the initial conductivity, $\sigma_n$ is the final conductivity and $\sigma_0$ is the apparent conductivity at time t, x, y, and z are the dimensions of the sample. Non-linear least square fitting is used to solve the diffusion equation and $D_{chem}$ and $D_{chem}$ are obtained as a solution. The program used to analyze the ECR data in this work is publicly available at NETL’s EDX server.6,36

Electrochemical impedance spectroscopy (EIS) was carried out on a two-electrode configuration symmetrical cells to test the electrochemical performance of BFCZ using CDE dense pellets (Fuel Cell Materials Co.) as electrolyte. A painting slurry was prepared by mixing the BFCZ powders and commercial Sm$_2$O$_3$Ce$_{0.8}$O$_{1.9}$ (SDC) (La$_{0.6}$Sr$_{0.4}$O$_{1.9}$, Ce$_{0.8}$Fe$_{0.2}$O$_{1.9}$ (LSCF) and La$_{0.8}$Sr$_{0.2}$O$_{1.9}$Mn$_{0.2}$O$_{1.9}$ (LSM) (Fuel Cell Materials Co.) powders with a commercial organic vehicle (Fuel Cell Materials Co.) was used for coating thin layers before a final firing step (1050/1200°C, 3 h). A Solatron CellTest system (1470E+1455) was used to collect the impedance response.
system using three random arrangements of large 320-atom supercells and twelve random arrangements of small 40-atom supercells. The three 320-atom supercells arrangements for this material yielded an average energy above the convex hull of 72.9 meV per atom (standard deviation of 1.5 meV per atom) indicating only a very small dependence on the cation ordering. By comparison, the average energy above the convex hull of the 40-atom BFCZZ5 systems is 76.0 meV per atom (standard deviation of 6.8 meV per atom), very consistent with the 320-atom case but with a larger spread in values due to the more pronounced ordering of cations resulting from the use of a smaller supercell. Overall, these stability calculations are useful for qualitative insight on materials synthesis stability and long-term stability, and for assessing trends with composition.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
This project was funded by the United States Department of Energy, National Energy Technology Laboratory, in part, through a site support contract. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
R.J. and J.L. contributed equally to this work. J. Liu conducted material synthesis, XRD, EIS measurements, and ECR measurements. R. Jacobs conducted the DFT calculations. R. Jacobs and J. Liu wrote and reviewed the manuscript. B. Guan fabricated the composite electrode cells. B.-t. Na conducted the long-term ECR measurements. S. Lee conducted button cell infiltration tests. H. Abernathy, D. Morgan, G. Hackett, and T. Kalapos conceived of and supervised the project. All authors reviewed, edited, and approved the manuscript prior to submission.

Data Availability Statement
The data that support the findings of this study are openly available in Figshare at 10.6084/m9.figshare.12515376, reference number [74].

Keywords
catalysis, density functional theory, oxygen reduction reaction, perovskites, SOFCs

Received: April 8, 2022
Published online: May 18, 2022

10mV AC perturbation over a frequency range of 1MHz to 10mHz. The test fixture was sealed in a quartz tube housing in a tube furnace for environment control. The temperature dependence of the polarization resistance was measured in air under 850, 800, 750, and 700 °C. The oxygen partial pressure dependence was measured in 10%, 20%, 40%, and 80% oxygen balanced with nitrogen controlled by gas-mixing panel equipped with digital mass-flow controllers (Alicat) allowed precise mixing from ultra-high purity N₂ and O₂. Area-specific resistance (ASR) values were determined by using the equivalent circuit model (Zview).

Density Functional Theory (DFT) Calculations: All density functional theory calculations were conducted using the Vienna Ab Initio simulation package (VASP) with a plane-wave basis set.[85] Calculations were performed using the Generalized Gradient Approximation (GGA) exchange and correlation functional with the Hubbard U correction (GGA+U)[86,87] with U values matching those used by the Materials Project database for accurate stability calculations.[88] Perdew–Burke–Ernzerhof (PBE) pseudopotentials were used.[89] All simulations were performed with spin polarization enabled. The total energy convergence was set to be about 1 meV per simulated cell. Planewave cutoff energies were set to be at least 30% higher than the highest cutoff for the applied pseudopotentials. All perovskite materials were simulated using 2 × 2 × 2 (40 atoms) supercells of the 1 × 1 × 1 (5 atoms) cubic perovskite unit cell, except for select cases where a larger 4 × 4 × 4 supercells (320 atoms) was used. Integration in the Brillouin zone was performed with the Monkhorst-Pack method with a 4 × 4 × 4 k-point mesh for all 2 × 2 × 2 supercells and a single k-point for the 4 × 4 × 4 supercells.[90] For each perovskite composition, the volume was first allowed to fully relax (symmetry disabled) to the most stable ground state. Given that these materials contain magnetically active Fe and Co, the total magnetic moment was scanned over a grid of approximately 1–3 μ₅ (depending on the particular case) above and below the value obtained from DFT for the first relaxation run in an effort to carefully detect the most stable total magnetic moment. Then, using the ground state volume and stable total magnetic moment, the cell parameters were changed to be pseudocubic, that is, a = b = c but with the same total volume as the fully relaxed run, and a subsequent second relaxation of ions only was performed.

The stability of each composition was calculated using the phase stability tools contained in the pymatgen package.[91] The stability value is represented as the energy above the convex hull (here, in units of meV per atom) of the multicomponent phase diagram formed by considering the total energies of all compounds contained in the composition space of interest. For example, calculating the stability of BaFe₀.₃Co₀.₃Zr₀.₇5O₃ constructs a phase diagram containing all binary, ternary, quaternary, etc. materials in the Ba–Fe–Co–Zr–O space, using the catalogued DFT total energies from the Materials Project database.[92] In this work, we are interested in the stability of BFCZ materials under typical SOFC operation conditions of T = 800 °C and p(O₂) = 0.2 atm. Thus, we conduct our stability calculations in a system open to O₂ gas, with an oxygen chemical potential of ~6.1 eV per O. This oxygen chemical potential value was obtained using standard DFT thermochemical equations as documented in previous studies.[93,94] Briefly, the chemical potential is calculated by shifting the DFT-calculated energy of an isolated O₂ molecule to account for finite temperature gas enthalpy and entropy effects using experimental tabulated data. The pressure dependence is included assuming O₂ behaves as an ideal gas. Vibrational free energy corrections are included assuming a basic Einstein model following previous work.[95,96] Finally, following previous work and the convention set by the materials project,[97] the shift of the O₂ energy to correct for systematic errors of O₂ modeled with GGA-PBE to correctly obtain oxide formation energies is applied to the solid phase energies during the stability analysis, rather than to the O₂ gas chemical potential.

The structures of all BFCZ materials were constructed such that like-species on the B-site were arranged to be as far apart from each other as possible. Given we are working with a single 40-atom supercell for each BFCZ composition which has a particular cation ordering associated with it, there is expected to be variation in the calculated stability based on the chosen arrangement of cations. To investigate the scale of this effect, we conducted a test of calculating the stability of the BFCZ25...
