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

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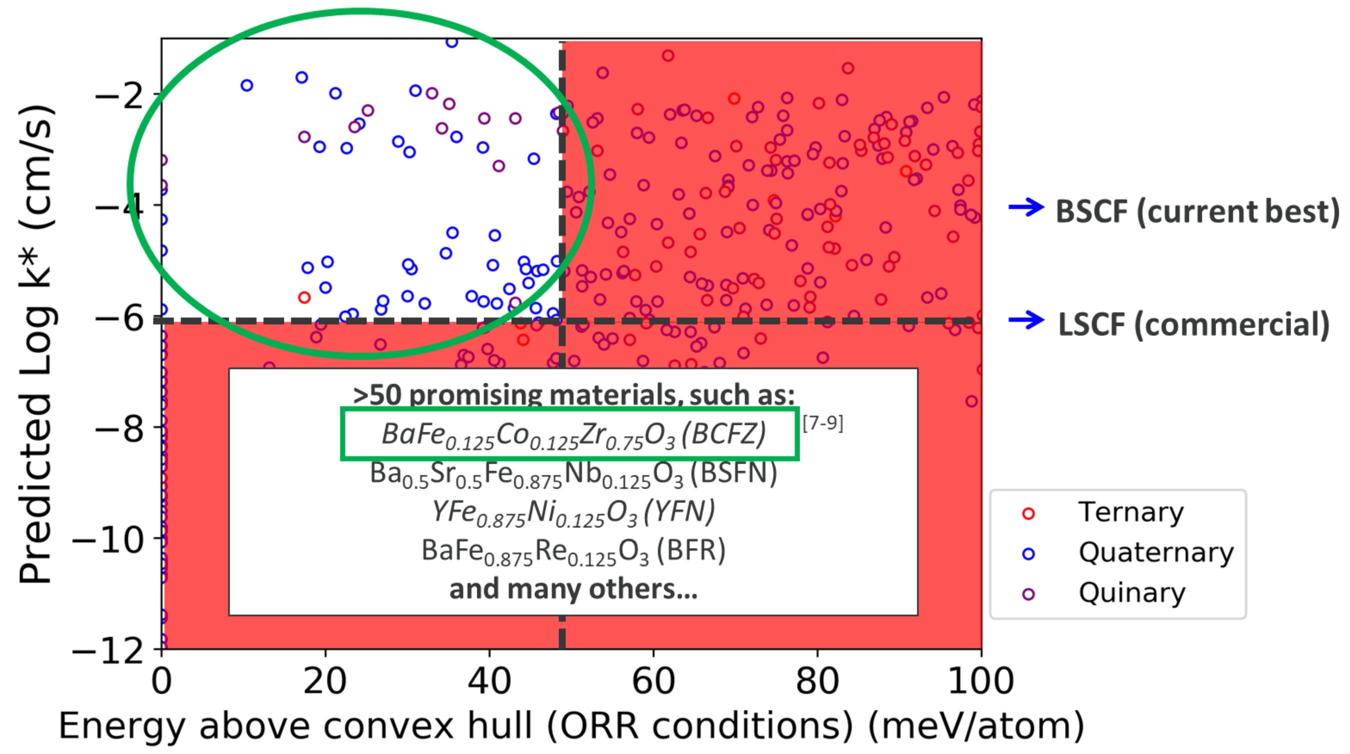
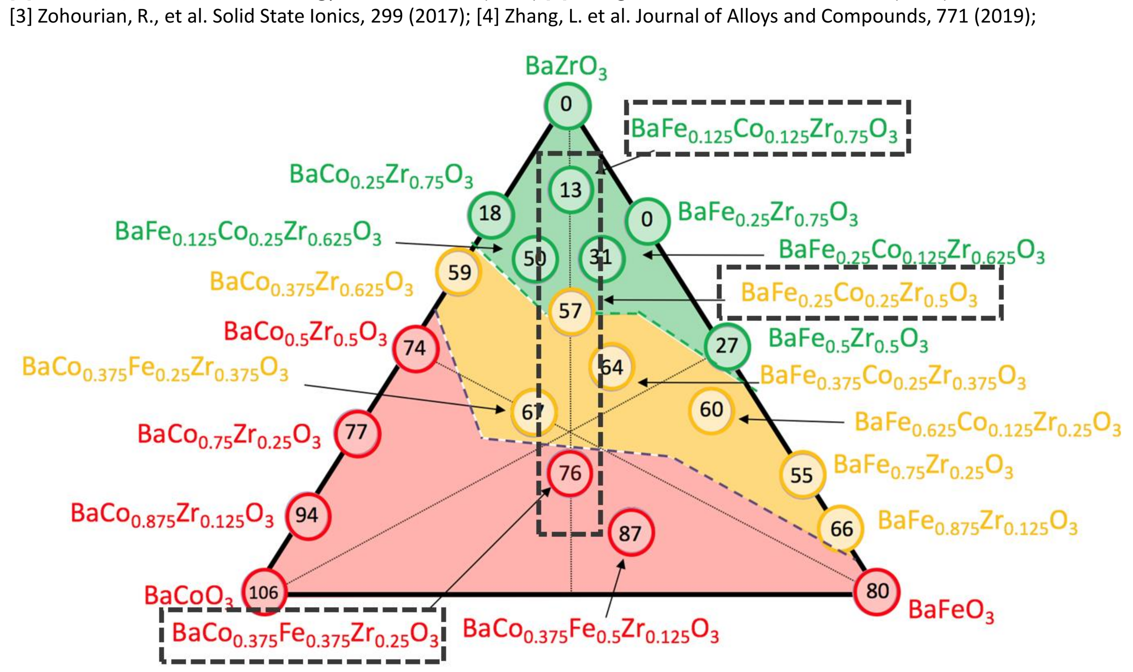
Introduction

- 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 $BaFe_{0.125}Co_{0.125}Zr_{0.75}O_3$ (BFCZ75), predicted to be promising from our recent density functional theory calculations and unconventional due to its extremely high Zr content and low electronic conductivity, exhibits oxygen reduction reaction surface exchange rates on par with $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ (BSCF) and excellent stability at typical operating temperatures. We engineer new composite electrodes integrating BFCZ75 with commercial electrode materials $La_{1-x}Sr_xMnO_3$ (LSM) and $La_{1-x}Sr_xCo_yFe_{1-y}O_3$ (LSCF) and achieve high performance as measured by low area specific resistance (ASR) values.

DFT Predicted Stability and Activity



[1] Jacobs, R., et al., Advanced Energy Materials, 8, 11 (2018);[2] Shang, M. et al. RSC Advances, 3, 36 (2013);
[3] Zohourian, R., et al. Solid State Ionics, 299 (2017); [4] Zhang, L. et al. Journal of Alloys and Compounds, 771 (2019);

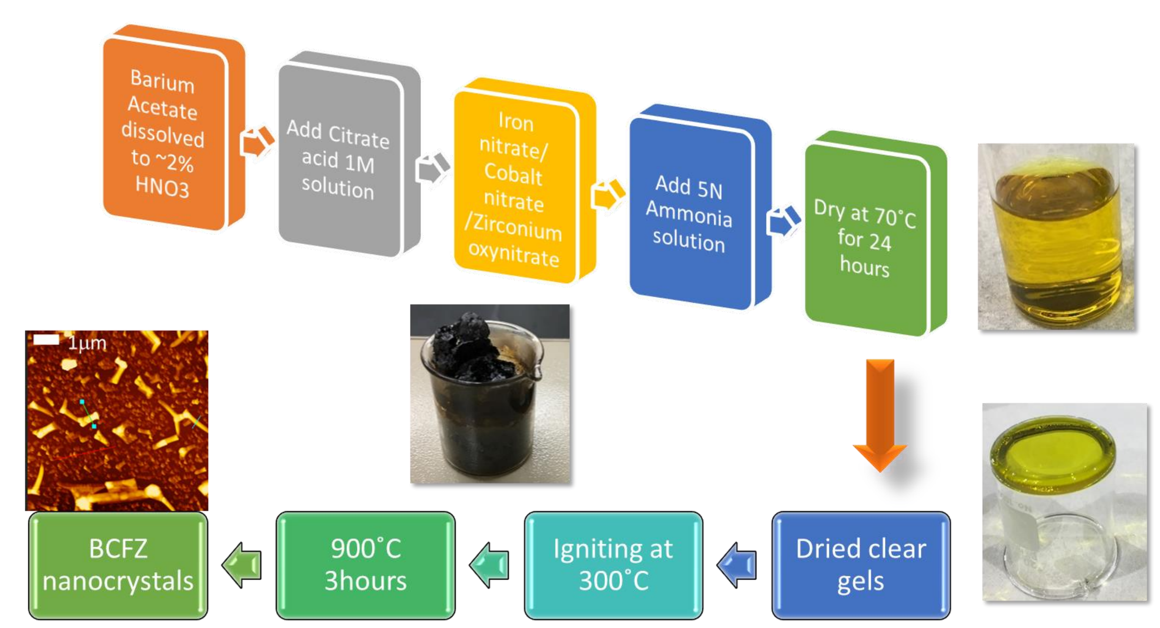


Computational stability ranking (from DFT and convex hull analysis):
BFCZ75>BFCZ50>BFCZ25

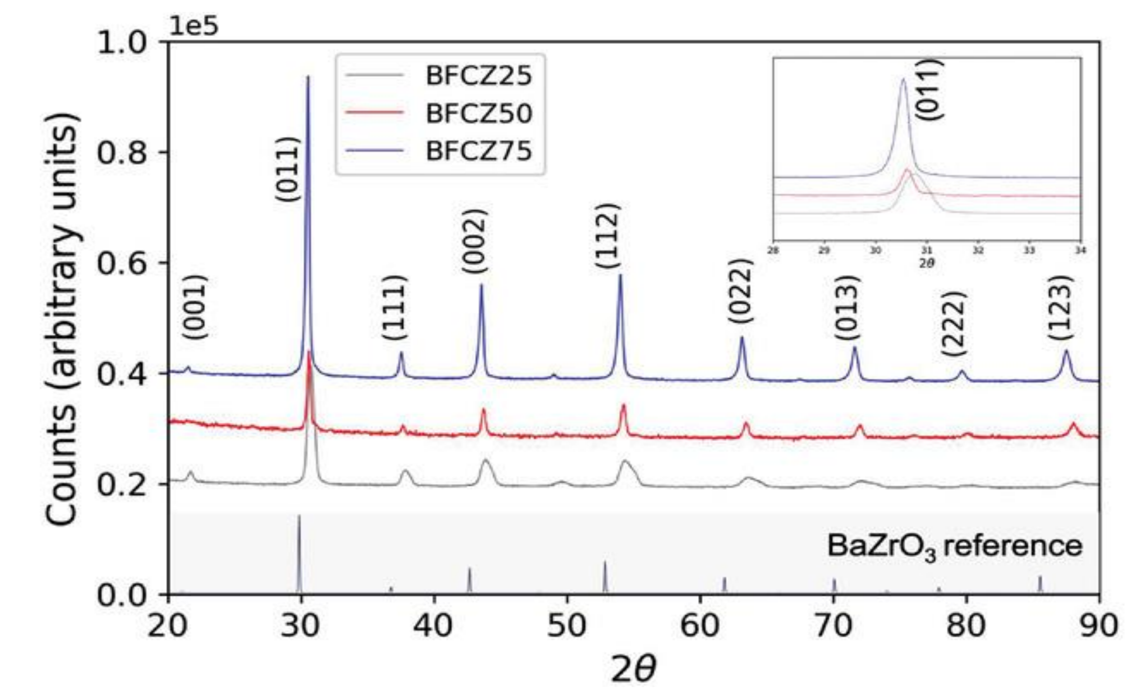
Calculated ternary stability map showing trends to DFT-calculated stability, illustrated here as energies above the convex hull in units of meV/atom under typical SOFC operating conditions (T=800° C, pO_2=0.2 atm). Black dashed boxes indicate BFCZ material compositions selected for experimental evaluation in this work. For the composition $BaCo_{0.375}Fe_{0.375}Zr_{0.25}O_3$, the energy above 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.

Results

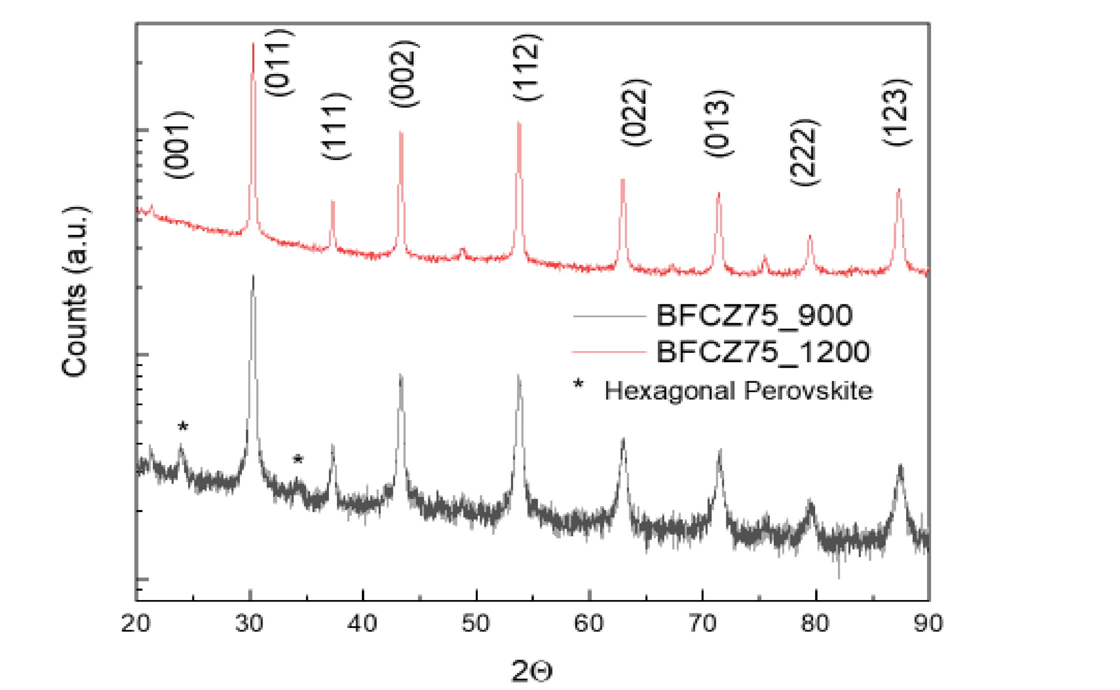
Synthesis of BFCZ phases and characterization



Synthesis: Sol-gel combustion

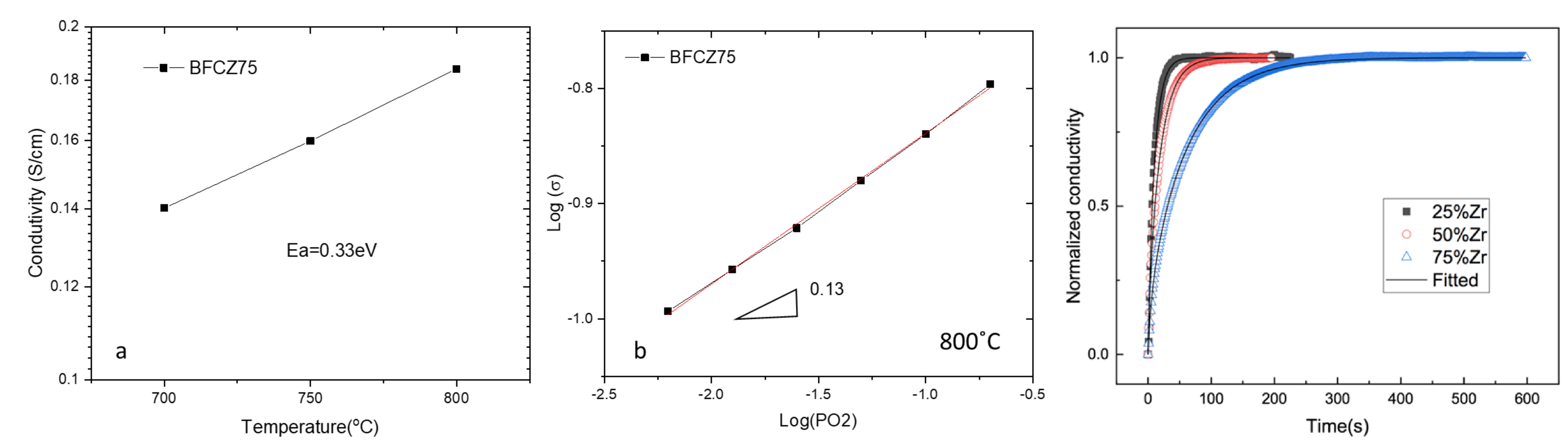


Powder XRD patterns of BFCZ materials showing that synthesis of BFCZ25 (black), BFCZ50 (red) and BFCZ75 (blue) all exhibit the cubic perovskite structure.



After calcining at 900˚C the BFCZ75 has formed cubic perovskite phase with the hint of a small amount a hexagonal perovskite structure like α-$BaTiO_3$ with lattice parameters a~5.22A and c~12.82A.

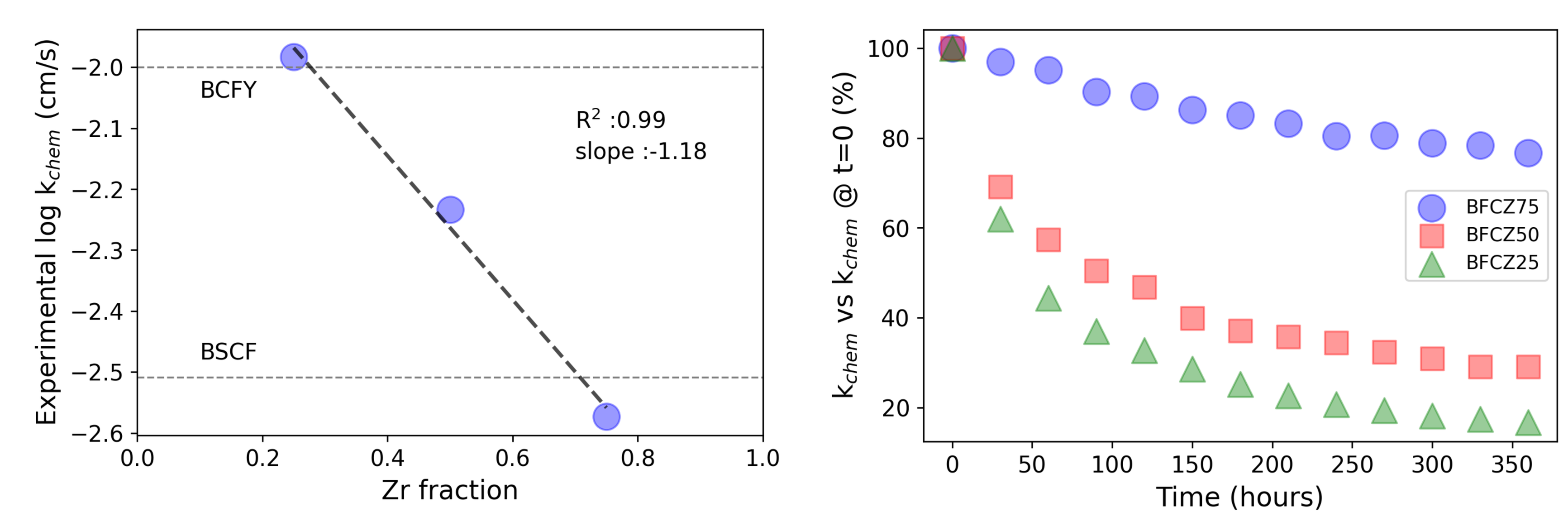
Electrical property and oxygen exchange activity



ECR-measured k_{chem} and D_{chem} values at 750° C

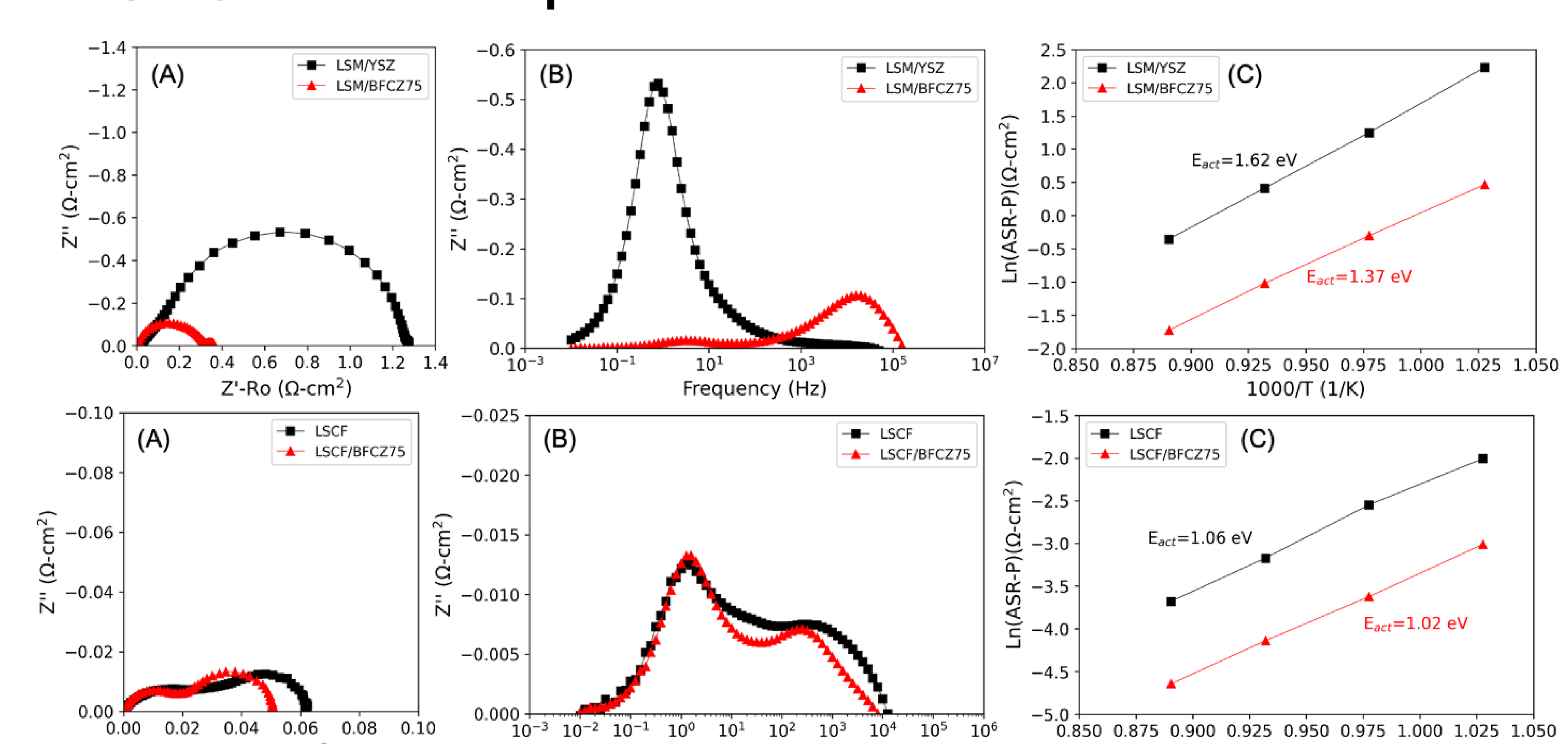
Material	k_{chem} (cm/s)	k_{chem} error (cm/s)	D_{chem} (cm²/s)	D_{chem} error (cm²/s)
BFCZ25	1.04×10^{-2}	$\pm 4.02 \times 10^{-4}$	2.06×10^{-4}	$\pm 1.35 \times 10^{-5}$
BFCZ50	5.84×10^{-3}	$\pm 1.08 \times 10^{-4}$	6.92×10^{-6}	$\pm 1.64 \times 10^{-8}$
BFCZ75	2.67×10^{-3}	$\pm 1.36 \times 10^{-4}$	8.66×10^{-6}	$\pm 2.66 \times 10^{-7}$
BSCF	3.33×10^{-3}	$\pm 2.73 \times 10^{-5}$	8.00×10^{-5}	$\pm 9.74 \times 10^{-7}$

Confirmation of model prediction



It is 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, confirming the value of increasing stability as opposed to just trying to optimize activity

BFCZ75 based composite electrodes



Summary

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 ceria based composite electrode, some stable composites contain a highly conductive material mixing 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 work is published in May 2022 issue of *Advanced Energy Materials*. https://doi.org/10.1002/aenm.202201203 -->)

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