

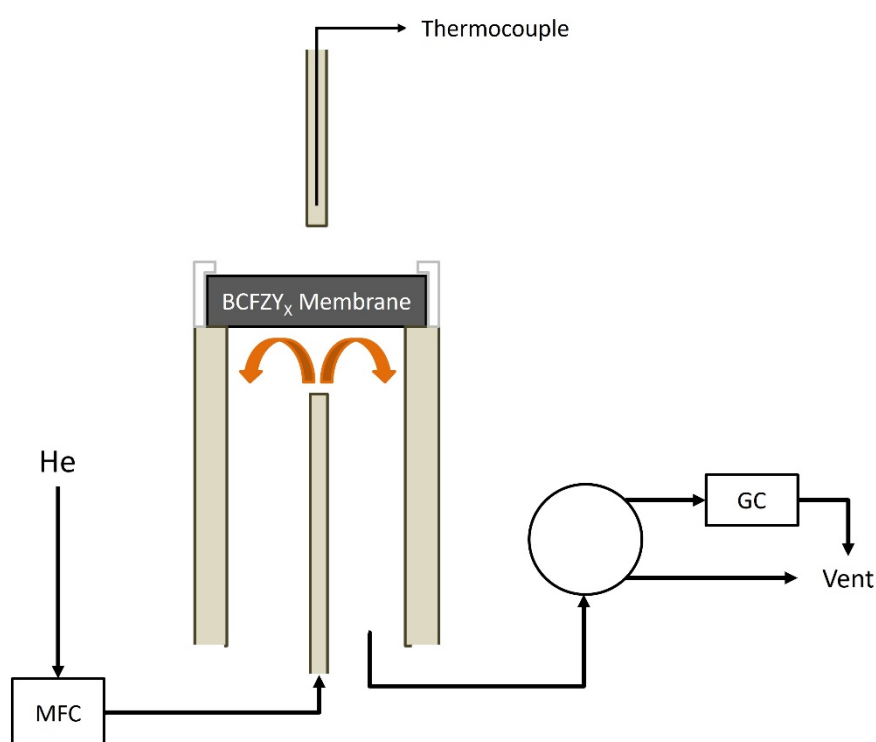
# Supplementary Materials: Surface and Bulk Oxygen Kinetics of $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2-x}\text{Y}_x\text{O}_{3-\delta}$ Triple Conducting Electrode Materials

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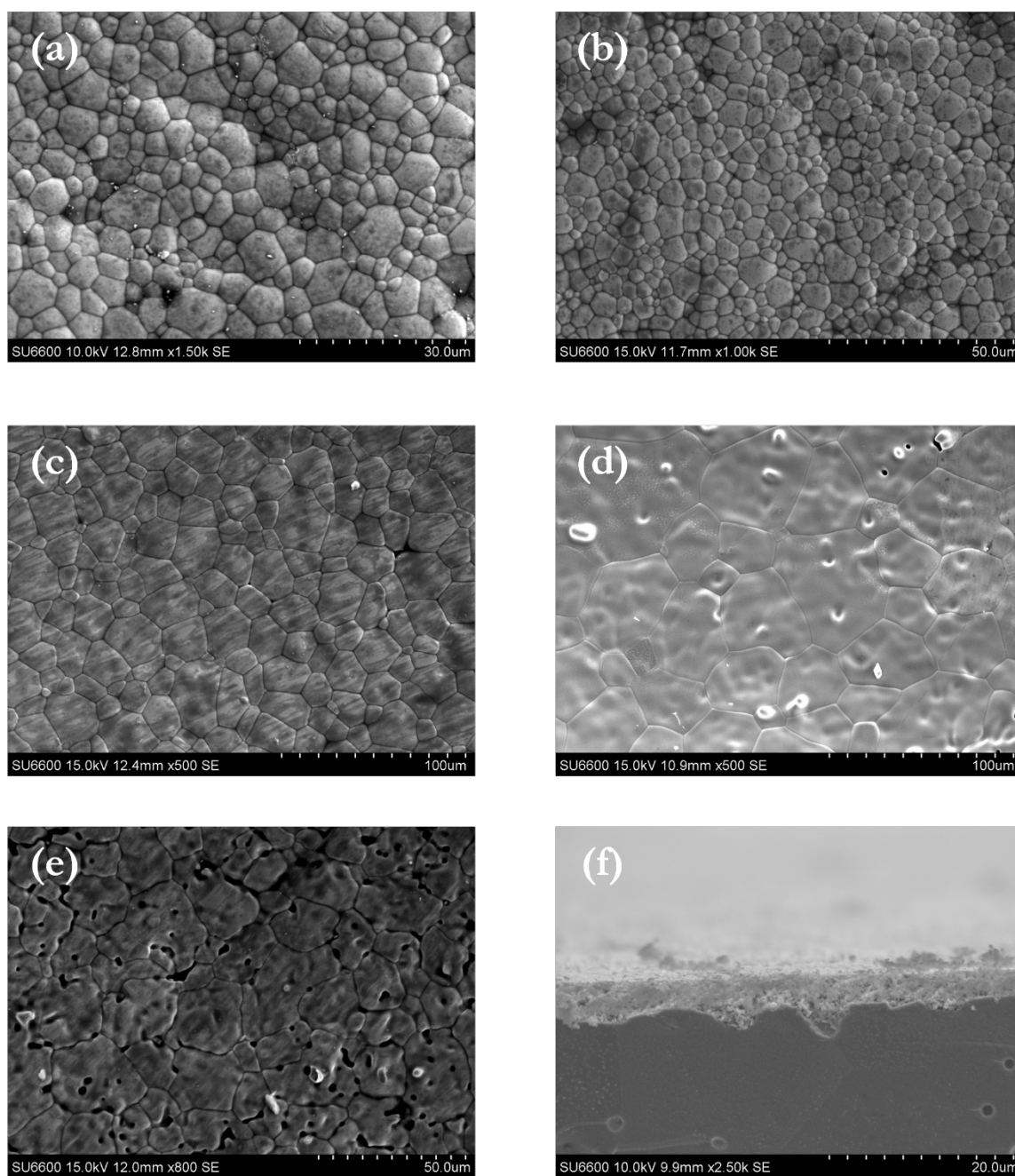
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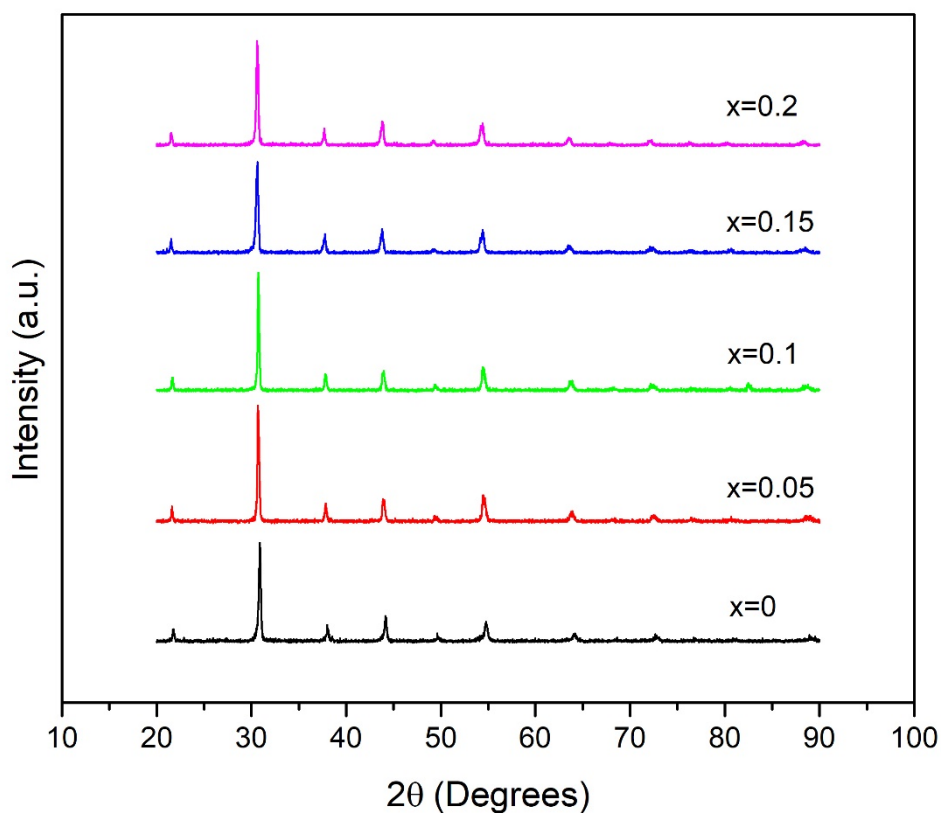
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**Figure S1.** Oxygen permeation experimental setup.



**Figure S2.** SEM images for BCFZY<sub>x</sub>, Surfaces for: (a) BCFZ, (b) BCFZY0.05, (c) BCFZY0.1, (d) BCFZY0.15, and (e) BCFY. Cross-section of: (f) BCFZY0.1 with surface coating.

Figure S3. BCFZY<sub>x</sub> X-Ray diffraction.Table S1. Estimated and calculated structural data for BCFZY<sub>x</sub>.

|                  | Estimated Lattice<br>Parameter (pm) <sup>1</sup> | Experimental Lattice<br>Parameter (pm) | Critical Radius (pm) <sup>2</sup> | Free Volume (Å <sup>3</sup> ) <sup>2</sup> | Average Metal-<br>Oxygen Bond<br>Energy (kJ/mol) <sup>3</sup> |
|------------------|--|--|-----------------------------------|--|---|
| <b>BCFZ</b>      | 409.2  | 411.7                                  | 82.48                             | 25.11                                      | -322.09   |
| <b>BCFZY0.05</b> | 411  | 412.8                                  | 82.74                             | 25.57                                      | -314.12   |
| <b>BCFZY0.1</b>  | 412.8  | 413.8                                  | 82.95                             | 25.98                                      | -306.15   |
| <b>BCFZY0.15</b> | 414.6  | 414                                    | 82.75                             | 25.98                                      | -298.18   |
| <b>BCFY</b>      | 416.4  | 414.5                                  | 82.7                              | 26.14                                      | -290.21   |

<sup>1</sup> Lattice parameter and estimated from literature-based ionic radii for given coordination number [1]

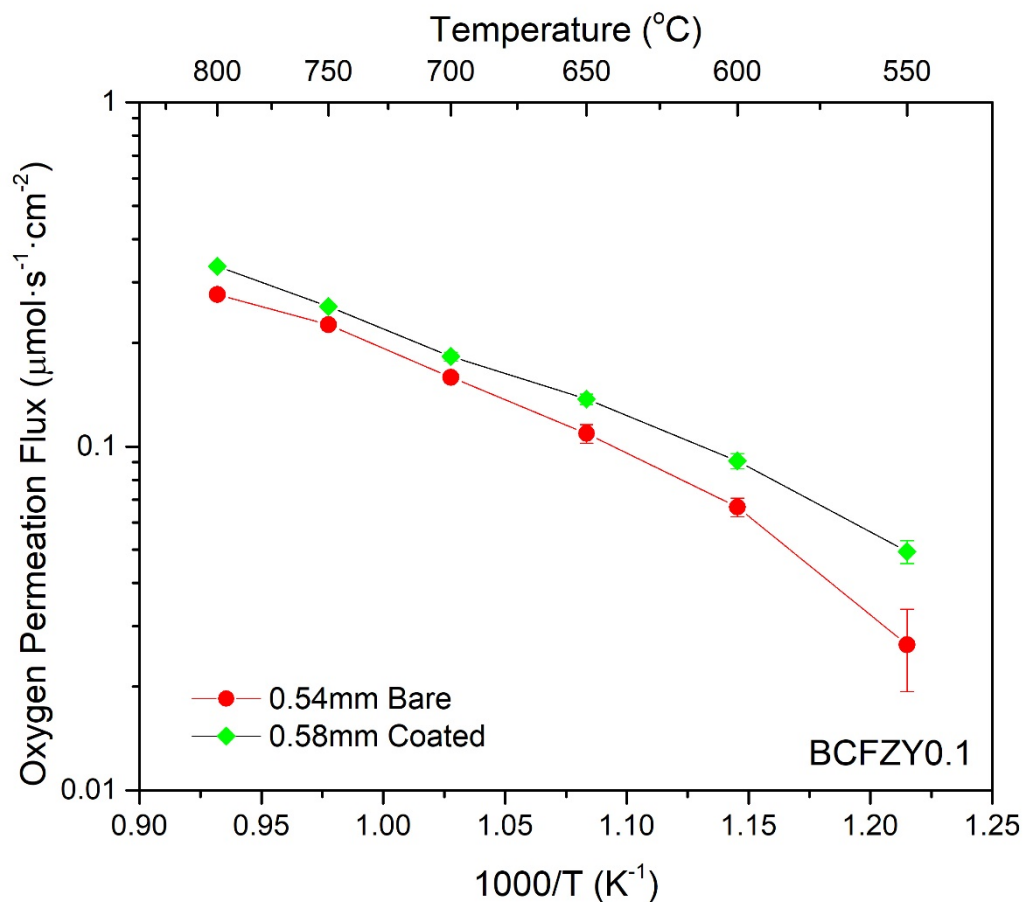
<sup>2</sup> Critical radius and free volume estimated using experimental lattice parameter and literature-based ionic radii [1,2]

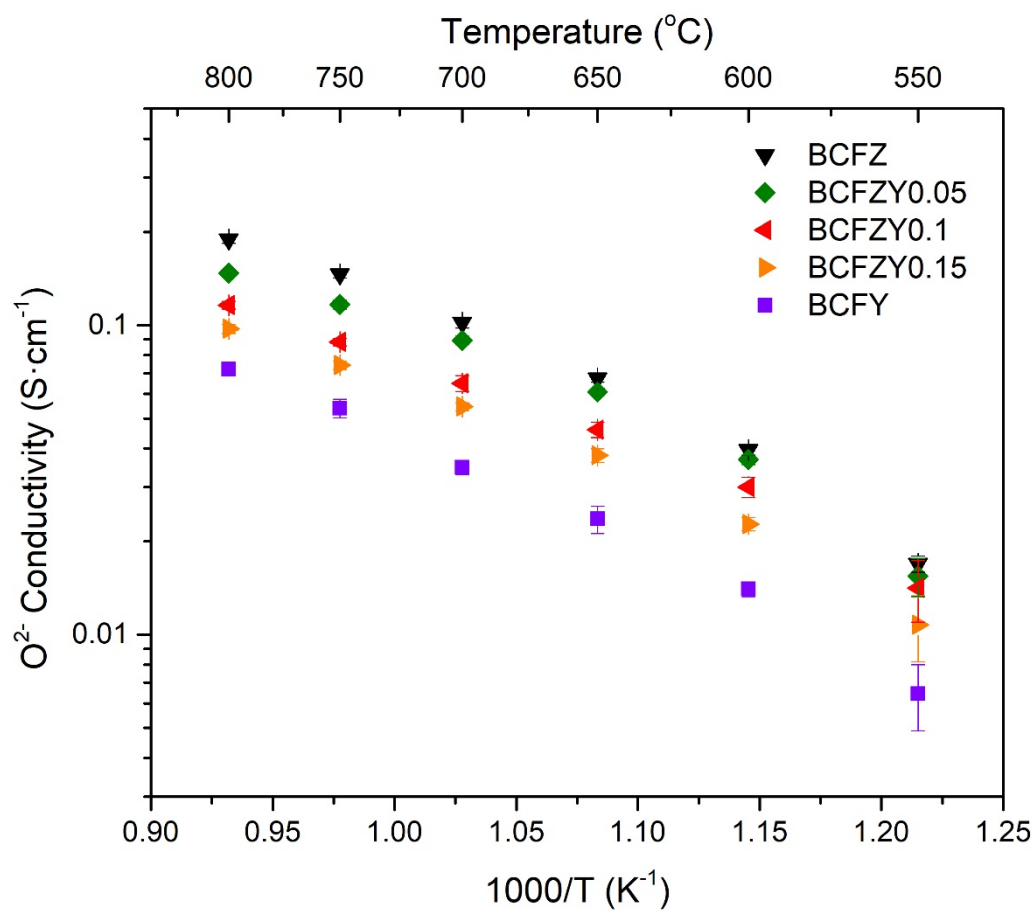
<sup>3</sup> Average metal-oxygen bond energy estimated from literature values [3].

**Table S2.** Stoichiometry of BCFZY<sub>x</sub> calculated from EDX data.

| Target Formula  | EDX Stoichiometry <sup>1</sup>   |
|---|--|
| BaCo <sub>0.4</sub> Fe <sub>0.4</sub> Zr <sub>0.2</sub> O <sub>3-δ</sub>                    | Ba <sub>1.29</sub> Co <sub>0.43</sub> Fe <sub>0.47</sub> Zr <sub>0.2</sub>                       |
| BaCo <sub>0.4</sub> Fe <sub>0.4</sub> Zr <sub>0.15</sub> Y <sub>0.05</sub> O <sub>3-δ</sub> | Ba <sub>1.33</sub> Co <sub>0.414</sub> Fe <sub>0.398</sub> Zr <sub>0.15</sub> Y <sub>0.047</sub> |
| aCo <sub>0.4</sub> Fe <sub>0.4</sub> Zr <sub>0.1</sub> Y <sub>0.1</sub> O <sub>3-δ</sub>    | Ba <sub>1.37</sub> Co <sub>0.434</sub> Fe <sub>0.406</sub> Zr <sub>0.1</sub> Y <sub>0.097</sub>  |
| BaCo <sub>0.4</sub> Fe <sub>0.4</sub> Zr <sub>0.05</sub> Y <sub>0.15</sub> O <sub>3-δ</sub> | Ba <sub>1.31</sub> Co <sub>0.418</sub> Fe <sub>0.401</sub> Zr <sub>0.05</sub> Y <sub>0.148</sub> |
| BaCo <sub>0.4</sub> Fe <sub>0.4</sub> Y <sub>0.2</sub> O <sub>3-δ</sub>                     | Ba <sub>1.49</sub> Co <sub>0.55</sub> Fe <sub>0.55</sub> Y <sub>0.2</sub>                        |

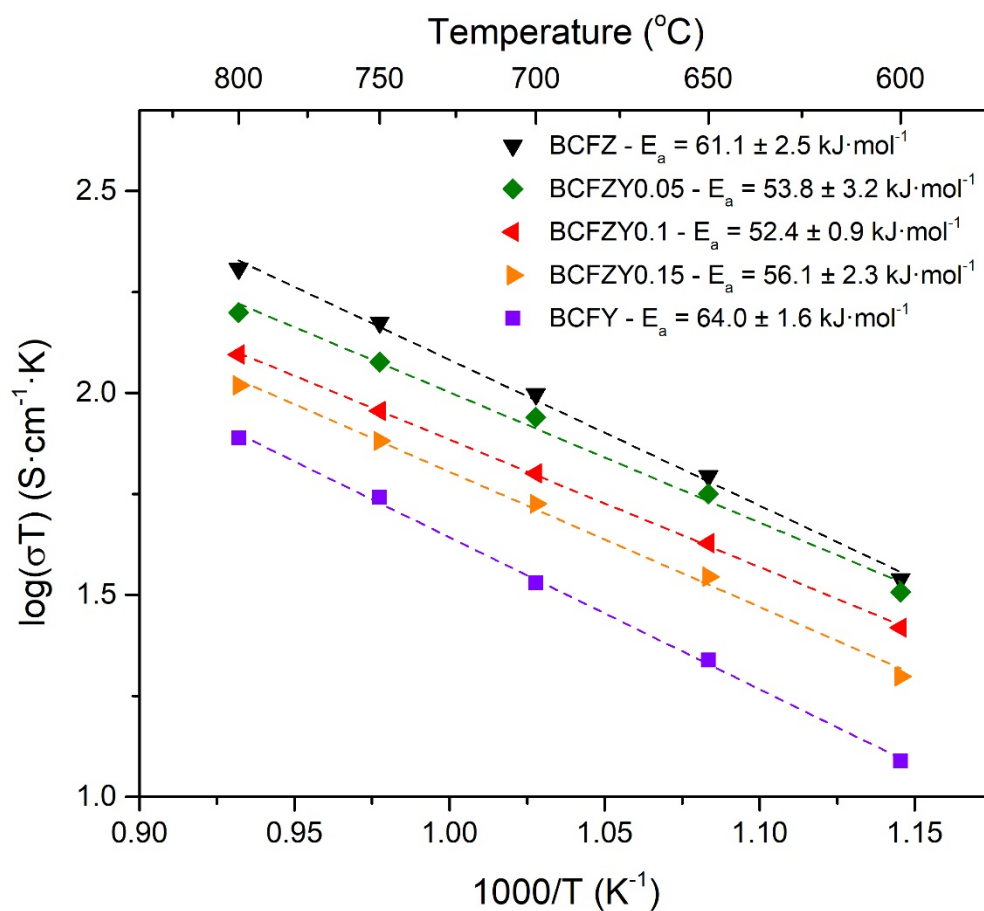
<sup>1</sup> EDX stoichiometry normalized to Zr ion in BCFZ, BCFZY0.05, BCFZY0.1, BCFZY0.15, and to Y ion in BCFY.

**Figure S4.** Oxygen permeation flux for bare and surface-coated membranes.



**Figure S5.** Oxygen ion conductivity as a function of temperature.

Oxygen ion conductivity estimated using the Wagner equation with the assumption that BCFZY<sub>x</sub> membranes are bulk-limited.



**Figure S6.** Arrhenius plot of oxygen conductivity for BCFZY<sub>x</sub>.

## References

1. Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767, doi:10.1107/S0567739476001551.
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