

**Innovative Approaches to Decarbonization:  
Synthesis of Carbon Nanotubes from CO<sub>2</sub> and Engineering Proton-Conducting Solid Oxide  
Electrolyzers for Clean Hydrogen Production**

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Rising anthropogenic greenhouse gas (GHG) emissions pose severe risks to economic stability, environmental integrity, and human health, making the development of decarbonization technologies imperative. The electricity generation sector has already experienced a massive 20-year transformation, with solar and onshore wind installations now demonstrably cheaper than natural gas and coal-fired power plants across most US and global markets. Consequently, electrochemical CO<sub>2</sub> reduction and clean hydrogen production have emerged as two promising decarbonization strategies that can leverage this inexpensive clean electricity to offset GHG emissions in hard-to-abate sectors such as heavy transportation and industry. However, critical technological challenges persist, limiting the affordability and reliability of traditional CO<sub>2</sub> and H<sub>2</sub>O electrolyzers. This dissertation successfully advances tandem electro-thermochemical carbon nanotube production from CO<sub>2</sub> and proton-conducting solid oxide water electrolyzers (p-SOECs) as innovative decarbonization approaches to address these critical challenges.

This dissertation first addresses the lack of an economically viable product from electrochemical CO<sub>2</sub> reduction. Solid carbon is an enticing CO<sub>2</sub> derivative due to its high sequestration potential, straightforward transportation, and ability to be processed into high-value composite materials. However, directly producing solid carbon in a low-temperature CO<sub>2</sub> electrolyzer is not practical due to unfavorable thermodynamics and durability concerns. We overcome this challenge by designing a tandem electro-thermochemical system. This system couples economically viable electrochemical reduction of CO<sub>2</sub> to CO with thermochemical reduction of CO to carbon nanotubes (CNTs), which are subsequently processed and 3D printed into high-density carbon nanocomposites. By carefully tuning the CO<sub>2</sub> residence time in the electrolyzer, we achieved an optimal feed gas for thermochemical CO reduction. The integrated process was operated stably for over 45 hours, yielding 37 grams of CO<sub>2</sub>-derived CNTs. Carbon nanocomposites produced from these CO<sub>2</sub>-derived CNTs exhibit exceptional material properties, with a Young's modulus of 1.61 GPa. Finally, we show that this novel process offers vast economic and decarbonization potential driven by the projected growth in carbon composite demand.

This dissertation then investigates electrochemical clean hydrogen production in p-SOECs. p-SOECs hold tremendous potential for affordable clean hydrogen production thanks to inherent advantages presented by their intermediate temperature operation (350-600 °C). This temperature regime enables the use of earth-abundant materials and decreases electricity consumption versus low-temperature (<100 °C) electrolyzers while easing material interdiffusion issues and high balance of plant costs characteristic of high-temperature (>700 °C) electrolyzers. However, with existing materials and cell designs, p-SOECs which simultaneously exhibit high performance, Faradaic efficiency, and durability have remained elusive, largely due to challenges associated with electronic leakage, insufficient oxygen evolution reaction (OER) activity, and materials degradation.

We first developed  $\text{BaZr}_{0.6}\text{Sc}_{0.4}\text{O}_{3-\delta}$  (BZSc40) as an advanced p-SOEC electrolyte. p-SOECs employing BZSc40 electrolytes demonstrated superior current densities (-0.85 A/cm<sup>2</sup> vs. -0.64 A/cm<sup>2</sup> at 1.3 V and 600 °C) and Faradaic efficiencies (76% vs. 54% at -0.2 A/cm<sup>2</sup>) compared to relevant benchmarks. Computational modeling revealed that BZSc40's large oxygen vacancy concentration leads to elevated NiO diffusion during high-temperature sintering. We control this NiO diffusion to beneficial levels by optimizing the half-cell sintering temperature. Despite BZSc40 outperforming current benchmarks while displaying robust chemical stability, we report that further advancements are necessary to raise Faradaic efficiency to desirable levels.

We next present interlayer engineering as a transformative technique to address p-SOEC challenges. We demonstrate that introducing a thin (~0.8 μm) porous  $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$  (GDC) interlayer increases p-SOEC Faradaic efficiency from 63% to 81% at -0.8 A/cm<sup>2</sup> and 600 °C while decreasing polarization resistance ( $R_p$ ) from 0.54 to 0.28 Ω cm<sup>2</sup> at OCV. GDC interlayer p-SOECs display elevated effective H<sub>2</sub> current densities compared to control p-SOECs and reach up to -1.22 A/cm<sup>2</sup> at 1.3 V. Mechanistic studies on the interactions between GDC and BCZZ reveal that GDC intrinsically promotes OER kinetics by significantly reducing the polarization activation energy ( $E_{a_p}$ ), dropping from 1.45 to 1.22 eV for full p-SOECs and 0.98 to 0.76 eV for symmetric cells. This promotional effect is localized to the electrochemically active region of the oxygen electrode near the electrolyte interface. Durability testing for over 1500 hours under 50% H<sub>2</sub>O conditions indicates that the GDC interlayer also improves long-term stability, with a degradation rate 53% lower than control p-SOECs. These findings highlight the catalytic promoter role of GDC and establish interlayer engineering as a powerful strategy to enhance p-SOEC performance, Faradaic efficiency, and durability.