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# $\text{SrCo}_{0.8}\text{Nb}_{0.1}\text{Ta}_{0.1}\text{O}_{3-\delta}$ Based Cathodes for Electrolyte-Supported Proton-Conducting Solid Oxide Fuel Cells: Comparison with $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ Based Cathodes and Implications

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# SrCo<sub>0.8</sub>Nb<sub>0.1</sub>Ta<sub>0.1</sub>O<sub>3-δ</sub> Based Cathodes for Electrolyte-Supported Proton-Conducting Solid Oxide Fuel Cells: Comparison with Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> Based Cathodes and Implications

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Previous studies suggest that Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> (BSCF) demonstrates high water uptake in humidified air and mixed protonic and electronic conduction as the cathode for intermediate temperature (~400–600 °C) proton-conducting solid oxide fuel cells (PC-SOFC). However, whether such single phase mixed conducting cathodes would be optimal for the cathode oxygen reduction reaction (ORR) over PC-SOFC has not been well studied. In this research, another leading cathode material SrCo<sub>0.8</sub>Nb<sub>0.1</sub>Ta<sub>0.1</sub>O<sub>3-δ</sub> (SCNT) is investigated and compared with BSCF as the cathode for BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3</sub> (BZCYYb) electrolyte-supported PC-SOFC cells from 750 to 450 °C. The results show at intermediate temperature, pure SCNT displays negligible water uptake and lower performance than pure BSCF. On the other hand, SCNT-BZCYYb composite cathode perform better than both pure SCNT and pure BSCF, while BSCF-BZCYYb composite performs the worst. These observations suggest that the strong affinity to H<sub>2</sub>O for the single phase cathode of BSCF at intermediate temperature seems to inhibit oxygen adsorption and limits its performance as the cathode for PC-SOFC despite its mixed protonic and electronic conduction. In comparison, a composite cathode such as SCNT-BZCYYb might be more promising by enabling a better balance between the need for water absorption and proton conduction and the need for efficient oxygen adsorption/exchange.

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The cathode reaction rate has been considered as the major rate-limiting factor for proton conducting solid oxide fuel cell (PC-SOFC) operating at intermediate temperature (~400–600 °C).<sup>1–4</sup> So far, most of the cathode materials used for PC-SOFC are originally designed and evaluated based on conventional oxide-ion conducting SOFC (OC-SOFC).<sup>5–10</sup> In OC-SOFC, the additional oxide-ion conductivity in the cathode material usually benefits the cathode reaction process. For example, La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> (LSCF), which is a mixed oxide-ionic and electronic conductor,<sup>11–14</sup> shows improved cathode activity in OC-SOFC compared to electronic conductors such as silver, platinum, and La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> (LSM)<sup>15</sup> at temperature of ~750 °C and is often used by itself (as opposed to a composite) as the cathode for OC-SOFC.

However, as shown in earlier studies, pure LSCF cathode performed rather poorly on proton conducting cathode symmetrical cells especially at reduced temperature of 650 °C–450 °C.<sup>13</sup> It is only after adding a proton conducting ceramic electrolyte phase, for example, BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3</sub> (BZCYYb), to LSCF to make a composite cathode that made it much better with reduced polarization resistance.<sup>13,16</sup> On the other hand, Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> (BSCF) is another mixed oxide-ionic and electronic conductor widely studied as cathode for OC-SOFC, especially at intermediate temperature. Our previous study on pure BSCF cathode symmetrical cells based on BZCYYb proton conducting electrolyte showed much better performance than pure LSCF cathode.<sup>13</sup> The much higher activity for pure BSCF over pure LSCF as the cathode for PC-SOFC was attributed to added proton conduction (apart from electronic conduction) in BSCF, which is enabled by significant water uptake/hydration of BSCF under humidified condition and resulting protonic defect formation from oxygen vacancy in BSCF.<sup>17,18</sup>

However, despite those studies, it is unclear whether a single phase mixed protonic and electronic conducting material with strong hydration such as BSCF would be ideal as cathode for PC-SOFC, especially at intermediate temperature. Part of this uncertainty comes from the fact that, at intermediate temperature such as

~550 °C or lower, the LSCF cathode material used for comparison in previous study has very limited oxide ion conductivity and performs significantly worse than pure BSCF even for OC-SOFC (with doped ceria electrolyte).<sup>8,19</sup> Thus, in this study, one of the most-recently developed leading mixed oxide-ionic and electronic conducting cathode material—SrCo<sub>0.8</sub>Nb<sub>0.1</sub>Ta<sub>0.1</sub>O<sub>3-δ</sub> (SCNT), which shows significantly better performance than pure BSCF cathode on OC-SOFC at intermediate temperature (e.g., ~0.7 W cm<sup>-2</sup> for SCNT<sup>20</sup> vs ~0.2 W cm<sup>-2</sup> for BSCF<sup>19</sup> over the same Gd<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.95</sub> or GDC electrolyte at 450 °C), was studied as the cathode material for BZCYYb electrolyte-supported PC-SOFC. The rationale to choose SCNT as the cathode material was to maintain high oxide-ion conductivity while suppressing proton conduction by avoiding the strongly-basic Ba element and associated high water affinity in the cathode. The cathode activity (in terms of cell electrochemical impedance and current-voltage characteristics) for pure SCNT cathode as well as SCNT-BZCYYb composite cathode was studied and compared with both pure BSCF and BSCF-BZCYYb composite cathodes over electrolyte-supported PC-SOFC button cells at 750 °C–450 °C. The implications of the observations are discussed and the directions for designing cathodes for PC-SOFC operating at intermediate temperature are pointed out.

## Experimental

**Powder synthesis.**—In this study, powders of the BZCYYb electrolyte (nominal composition of BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3-δ</sub>) and the BSCF cathode (nominal composition of Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub>) were synthesized by the combustion process followed by heat treatments, which have been described before.<sup>21</sup> The SCNT was synthesized through a solid state reaction route as described in literature.<sup>20</sup> Briefly, stoichiometric amounts of SrCO<sub>3</sub> (99.9%, Aldrich), Co<sub>3</sub>O<sub>4</sub> (99.9%, Aldrich), Nb<sub>2</sub>O<sub>5</sub> (99.9%, Aldrich) and Ta<sub>2</sub>O<sub>5</sub> (99.9%, Aldrich) were mixed by ball-milling for 24 h, followed by pelletizing and reaction in air at 1200 °C for 10 h. After that, the pellets were ground into powder, pressed into pellets again, and reacted at 1200 °C for another 12 h. The as-synthesized SCNT powder was analyzed by X-ray diffraction (SIEMENS diffractometer D5000) for phase identification.

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**Thermogravimetric analysis (TGA).**—To determine the hydration property (or water uptake) of SCNT, TGA was carried out on pre-hydrated SCNT loose powder. To prepare for the TGA experiment, the as-synthesized SCNT powder was heated up to 1000 °C in dry simulated air (a gas mixture of 20% O<sub>2</sub> and 80% N<sub>2</sub>, Airgas with negligible moisture) and then cooled in 10% wet simulated air ( $p_{\text{H}_2\text{O}} \approx 0.10$  bar, as obtained by bubbling the simulated air through water maintained at  $\sim 45$  °C) from 1000 °C down to 500 °C at a rate of 0.5 °C min<sup>-1</sup>, followed by dwelling at 500 °C in the same 10% wet simulated air for 12 h and final slow cooling down to 150 °C at a rate of 0.5 °C min<sup>-1</sup>. The pre-hydrated SCNT powder sample was then characterized by TGA in dry air from room temperature to 1000 °C with heating and cooling rate of 1 °C min<sup>-1</sup>.<sup>17</sup>

**Cell fabrication and microstructure examination.**—Various electrolyte-supported button cells with BZCYYb electrolyte, Ni-BZCYYb cermet anode, and different BSCF or SCNT cathodes (including their composite cathodes) were fabricated. (In this study, electrolyte-supported cells instead of anode-supported cells were used for electrochemical tests because the former gave better stability and robustness as well as higher open circuit voltage over long time that included thermal cycling.) First, electrolyte pellets with diameter of 10 mm were dry-pressed at 200 MPa using 0.2 g BZCYYb powder, followed by protected sintering at 1550 °C in a muffle furnace in air for 5 h. The electrolyte thickness after sintering is  $\sim 400$   $\mu\text{m}$ . The anode was brush painted onto one side of the BZCYYb electrolyte pellet using a NiO-BZCYYb slurry (NiO: BZCYYb: organic vehicle weight ratio of 3: 2: 5).<sup>22</sup> The samples were dried and calcined in air at 1400 °C for 2 h with heating and cooling rate of 5 °C min<sup>-1</sup>. Then, cathodes were brush painted onto the other side of the sintered BZCYYb pellets using different cathode slurries including pure BSCF, 70 wt% BSCF-30wt% BZCYYb mixture, pure SCNT, and 70 wt% SCNT-30wt% BZCYYb, respectively. (For all cathode slurries, the organic medium to total oxide powder weight ratio is kept at 1: 1.) All painted cathodes were dried in an air oven at 100 °C for 2 h and then calcined at 1000 °C for 2 h with heating and cooling rate of 5 °C min<sup>-1</sup>. The microstructure of the cathodes was examined using a field emission scanning electron microscope (FE-SEM, JEOL JSM 6330 F).

**Electrochemical measurements.**—Electrochemical Impedance Spectroscopy (EIS) and current-voltage (I-V) measurements were carried out using a potentiostat (Gamry Interface 1000). The cells were sealed onto one end of an alumina support tube using ceramic sealant (Aremco 552) and placed in the hot zone of a tube furnace. The cell was heated up to 750 °C during which the anode-side was purged with pure N<sub>2</sub> (UHP300 grade, Airgas) while the cathode side was exposed to ambient air. Then at 750 °C, the gas in the anode-side was switched to dry H<sub>2</sub> (UHP300 grade, Airgas) with a flow rate of 40 c.c. min<sup>-1</sup>, and NiO in the anode was reduced to Ni. After reduction,  $\sim 3$  vol% H<sub>2</sub>O was introduced to H<sub>2</sub> by passing the dry H<sub>2</sub> through a water bubbler at room temperature, while the cathode side was still exposed to ambient air. EIS (under open circuit condition)

and I-V curves for the different button cells were then collected at various temperatures between 750 and 450 °C.

## Results

**Phase analysis and microstructure of the cathodes.**—Figure 1 shows the XRD for synthesized SCNT powder. Cubic perovskite structure for SCNT was confirmed and matches literature.<sup>20</sup> The microstructure of fabricated pure SCNT, SCNT-BZCYYb composite, as well as pure BSCF, and BSCF-BZCYYb composite cathodes, all over the BZCYYb electrolyte are shown in Fig. 2. The thickness of all cathodes was typical  $\sim 20$ – $30$   $\mu\text{m}$ , and the porosities for SCNT, SCNT-BZCYYb, BSCF and BSCF-BZCYYb cathodes were estimated to be  $\sim 25\%$ ,  $\sim 30\%$ ,  $\sim 30\%$ , and  $\sim 25\%$ , respectively based on analysis of the cross-section SEM images using the software ImageJ (version 1.52). The pure BSCF and pure SCNT cathodes have similar large grain size of a few microns, while mixtures of coarse and finer particles are observed for both BSCF-BZCYYb and SCNT-BZCYYb composite cathodes. Those finer particles in the composite cathodes are BZCYYb proton conducting electrolyte phase, which requires much higher temperature for coarsening than SCNT or BSCF.

**TGA of pre-hydrated SCNT powder.**—The TGA result of pure SCNT powder after it was first heat treated at 500 °C in 10% wet simulated air for 12 h for water saturation (pre-hydration) is shown in Fig. 3. The TGA for pre-hydrated LSCF and pre-hydrated BSCF from Grimaud's study<sup>17</sup> are also replotted in Fig. 3 for comparison. For pre-hydrated SCNT powder, it loses weight linearly up to 1.1 wt% during the heating-up in dry air to 1000 °C due to the loss of lattice oxygen and formation of more oxygen vacancy; it regains weight during the cooling-down due to re-absorption of oxygen and filling up of the oxygen vacancies. No significant difference or hysteresis between the heating-up and the cooling-down at temperature above  $\sim 400$  °C was observed for the pre-hydrated SCNT powder, indicating that the SCNT material has negligible hydration (or water absorption) capability.<sup>17</sup> The absence of hysteresis in TGA traces above  $\sim 400$  °C for pre-hydrated SCNT is similar to pre-hydrated LSCF, as reported by Grimaud (replotted in Fig. 3).<sup>17</sup> In comparison, for pre-hydrated BSCF (also replotted in Fig. 3), Grimaud reported that, between the heating-up and the cooling-down, the difference in sample weight (or hysteresis) is very significant:  $\sim 0.8$  wt% at  $\sim 450$  °C, which corresponds to water up-take of 10 mol% at that temperature.<sup>17</sup> (It is noted that upon slow cooling to 300 °C and below, the SCNT sample weight increased to  $\sim 0.2$  wt% above the original. The exact reason for this is not clear at this moment, but it is unlikely to be related to hydration since the TGA including the cooling portion was carried out in dry air). The large difference in sample weight (or hysteresis) at  $\sim 450$  °C for BSCF between the heating trace and the cooling trace indicates strong water absorption for BSCF. Such a behavior is not observed for SCNT and LSCF.

**Electrochemical behaviors of different electrodes from 750 to 450 °C.**—Figure 4 shows the impedance spectra under open circuit

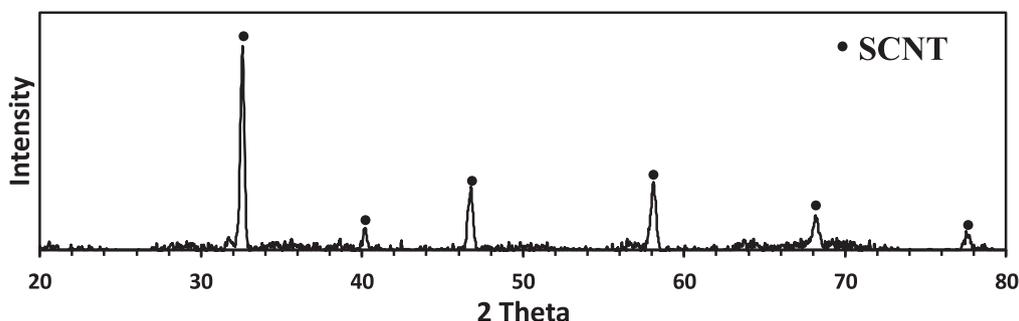
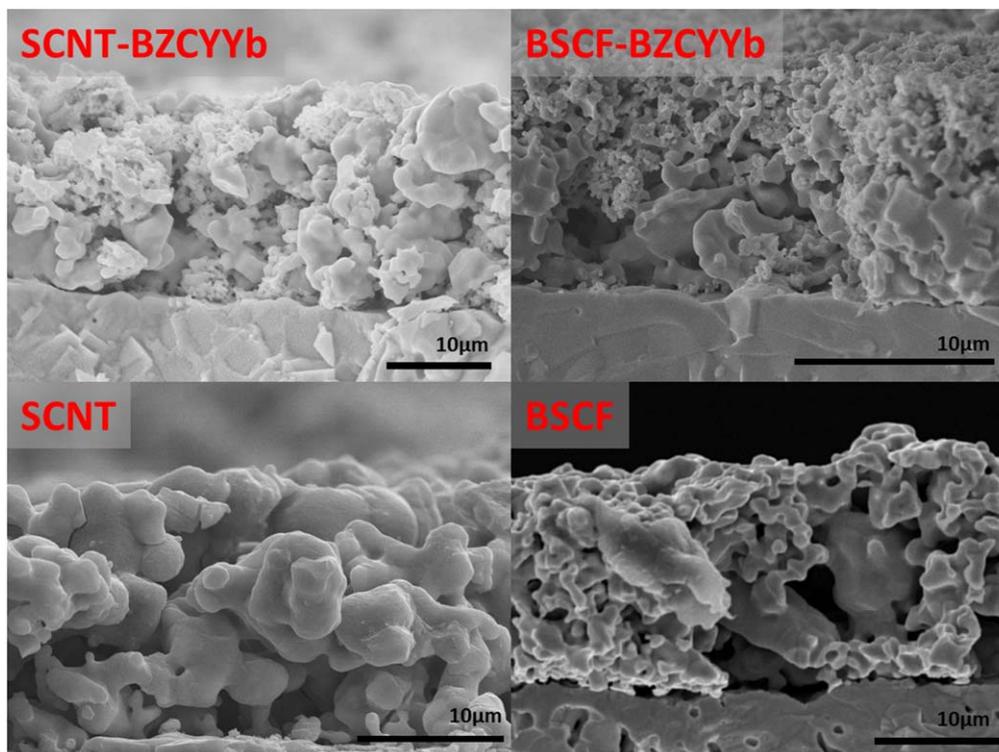
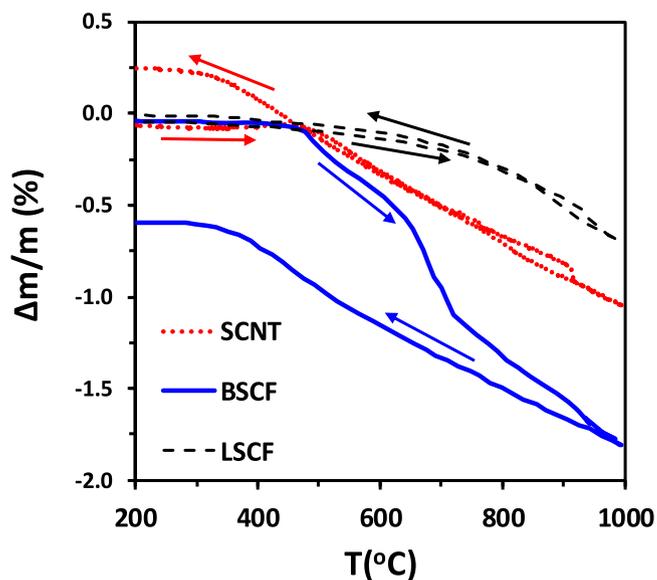


Figure 1. XRD pattern of the synthesized SCNT powder.



**Figure 2.** Microstructure of SCNT-BZCYYb, BSCF-BZCYYb, pure SCNT, and pure BSCF cathode on BZCYYb proton conducting electrolyte.

condition and current density - voltage/current density - power density ( $j - V/j - p$ ) curves for BZCYYb electrolyte-supported PC-SOFC button cells with various cathodes at 750 °C. The cell with SCNT-BZCYYb composite cathode shows the lowest polarization resistance ( $R_p$ ) and highest power density, while pure SCNT cathode shows slightly lower  $R_p$  and slightly higher power density than pure BSCF. On the other hand, the BSCF-BZCYYb composite cathode shows the highest  $R_p$  and lowest power density.



**Figure 3.** TGA of pre-hydrated SCNT powder (i.e., after 500 °C heat treatment in 10 vol% humidified air for 12 h for water saturation or pre-hydration, same for BSCF and LSCF) in comparison to pre-hydrated BSCF and LSCF (both replotted using data from an earlier study by Grimaud et al.<sup>17</sup>). The TGA was carried out by heating from room temperature to 1000 °C in dry air and then cooling down with heating and cooling rate of 1 °C min<sup>-1</sup>.

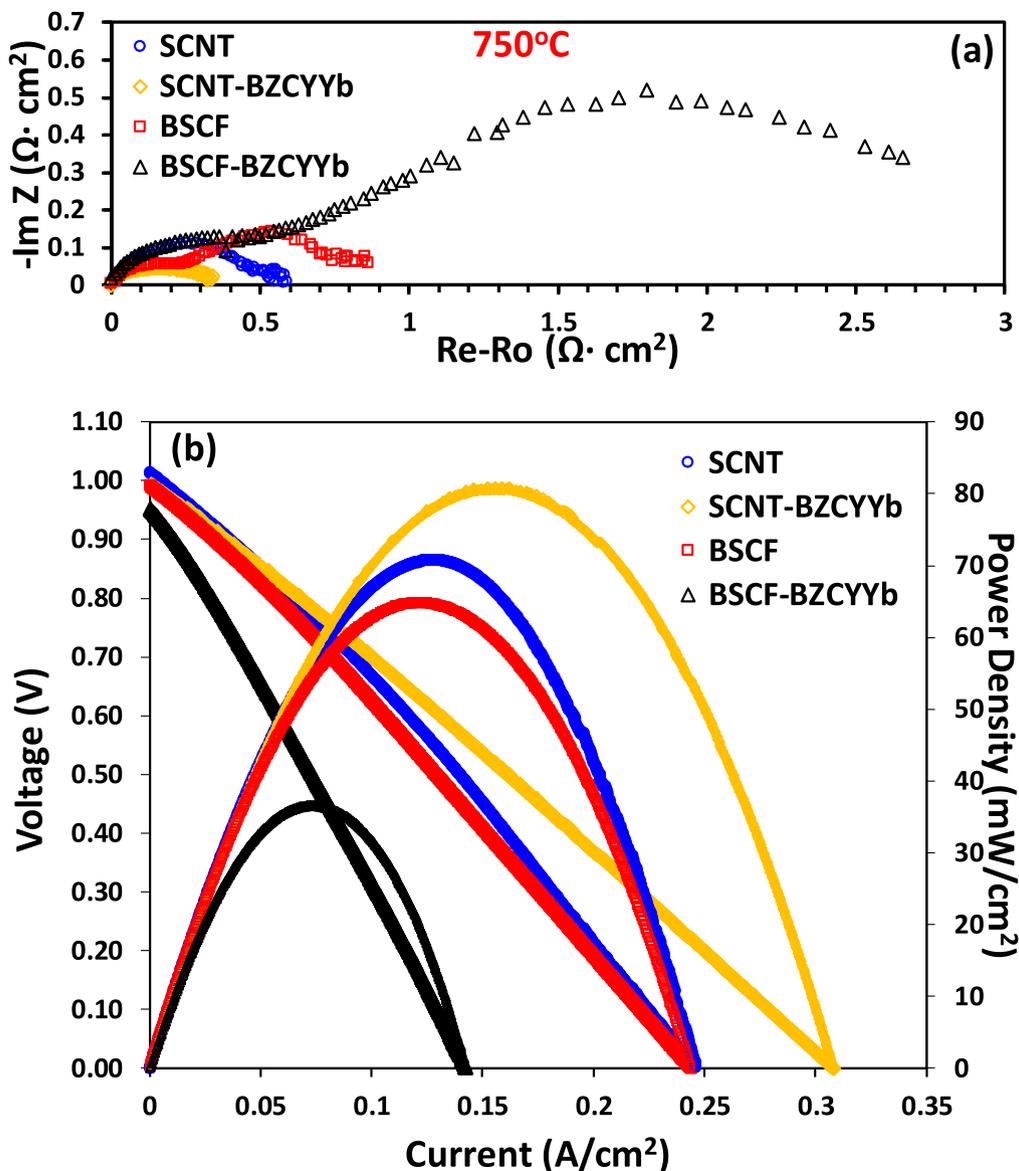
Figure 5 shows the impedance spectra and  $j - V/j - p$  curves for the various cells at reduced temperature of 650 °C. The cell with SCNT-BZCYYb composite cathode still shows the best performance with lowest  $R_p$  and highest power density, while BSCF-BZCYYb composite cathode remains the worst. On the other hand, the cell with pure SCNT cathode actually *underperforms* pure BSCF by showing higher  $R_p$  and lower power density than pure BSCF.

At further reduced temperature of 550 and 450 °C, the advantage of the cell with SCNT-BZCYYb composite cathode becomes even more significant, as shown in Fig. 6 and Fig. 7, while the cell with BSCF-BZCYYb composite cathode is still the worst. At the same time, the cell with pure BSCF cathode shows *much better* performance than pure SCNT as cathode for PC-SOFC: For example, at 550 °C,  $R_p$  for the pure BSCF cell is half of pure SCNT and max power density for pure BSCF cell doubles pure SCNT.

It should be noted that the cell performance reported here are all rather low, for example, ~2–13 mW at 450 °C, ~5–32 mW at 550 °C. One major reason for such low performance is related to the fact that all electrolyte-supported PC-SOFC have thick BZCYYb electrolyte of ~400 μm. As stated, such electrolyte-supported cells were used because they gave us better stability and robustness as well as high open circuit voltage (OCV), especially over longer time that included thermal cycling. The cell performance, although only on the mW scale at intermediate temperature, is actually consistent with expectation since previous studies have shown that SOFC (including PC-SOFC) performance could decrease by a factor of 15 or even more when comparing an anode-supported cell with 10 μm electrolyte to an electrolyte-supported cell with 500 μm electrolyte, both are based on the same materials set and have comparable processing conditions.<sup>23</sup> In addition, the electrodes' microstructure has not been optimized, which may also limit cell performance.

## Discussion

**General considerations for cathode oxygen reduction reaction for PC-SOFC vs conventional OC-SOFC.**—Before discussing the electrochemical behaviors for SCNT cathode and how it compares



**Figure 4.** Impedance spectra under open circuit condition (a) and current density-voltage/current density-power density ( $j - V/j - p$ ) curves (b) for BZCYYb electrolyte-supported PC-SOFC button cell with different cathodes of pure SCNT, SCNT-BZCYYb composite, pure BSCF, and BSCF-BZCYYb composite at 750 °C.

with other cathodes such as BSCF, some general considerations about cathode reaction for PC-SOFC vs conventional OC-SOFC are briefly re-captured here. As mentioned before in earlier researches,<sup>13,17,18,21</sup> the cathode oxygen reduction reaction (ORR) process in an ideal PC-SOFC will be



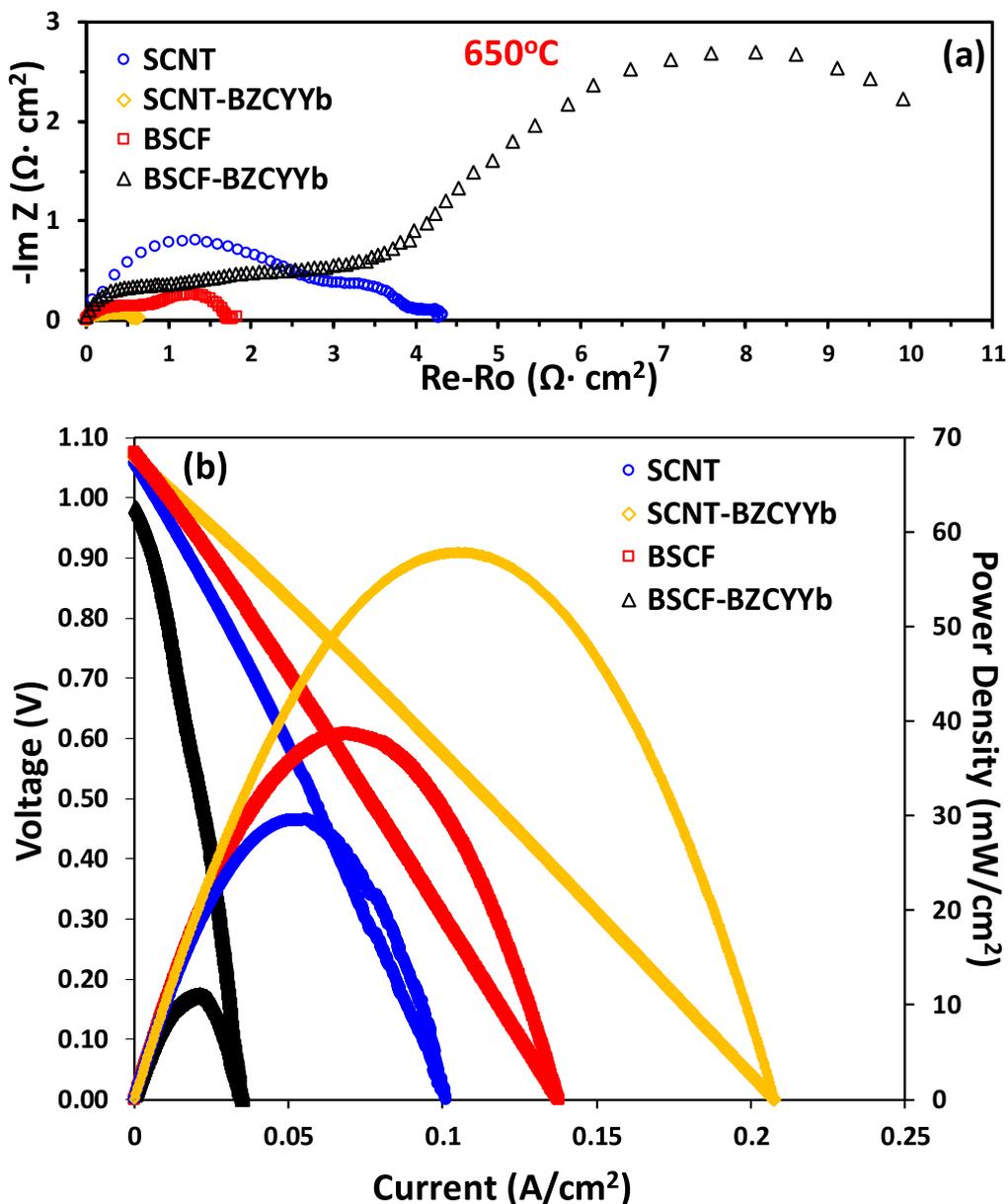
while the cathode ORR process in conventional OC-SOFC is usually written as



However, for practical PC-SOFC with a proton conducting electrolyte such as BZCYYb, when the temperature is relatively high ( $> \sim 700$  °C), the electrolyte might have significant oxide ion (i.e., oxygen vacancy  $\text{V}_{\text{O}}^{\bullet\bullet}$ ) conduction (as well as electronic conduction).<sup>2,24,25</sup> As a result, part of the cathode ORR of a nominal PC-SOFC at *elevated temperature* (e.g., 750 °C or above) might proceed via reaction **ii**, which has been confirmed by experiments.<sup>26</sup> Only when the temperature is reduced to  $\leq 650$  °C, especially 550 °C and lower, would proton conduction dominate, and the cathode reaction will mainly proceed through reaction **i**.<sup>27</sup>

As given before, Table I summarizes the elementary steps for both cathode reactions **i** and **ii**.<sup>13,18</sup> One major difference in the elementary steps for the cathode reaction **i** via the proton route vs reaction **ii** via oxide ion route is in the *charge transfer* step (step 3 vs 3', in Table I), while the elementary steps of oxygen adsorption (step 1) and dissociation (step 2) are expected to remain the same. Moreover, the mass transfer (step 4) of ionic species between the cathode and the electrolyte in the cathode reaction would also be different—oxide ion  $\text{V}_{\text{O}}^{\bullet\bullet}$  vs proton or protonated oxygen  $\text{OH}_{\text{O}}^{\bullet}$ . Finally, in cathode reaction **i** involving proton, there is an additional  $\text{H}_2\text{O}$  transport and desorption step (5'), which is absent in the cathode reaction **ii** for conventional pure OC-SOFC.

**Pure SCNT vs pure BSCF as cathode for PC-SOFC.**—As shown in Figs. 5–7, when temperature is in the range of  $\sim 650$ – $450$  °C, pure SCNT seems to *underperform* pure BSCF as the cathode for BZCYYb electrolyte-supported PC-SOFC button cells: the cells with pure SCNT cathode gives much higher  $R_p$  (under open circuit) and somewhat ( $\sim 20\%$ – $50\%$ ) lower power output than pure BSCF at all three temperatures of 650, 550, and 450 °C. (See also Fig. 8a for a direct comparison.) In fact, closer examination of the EIS for the



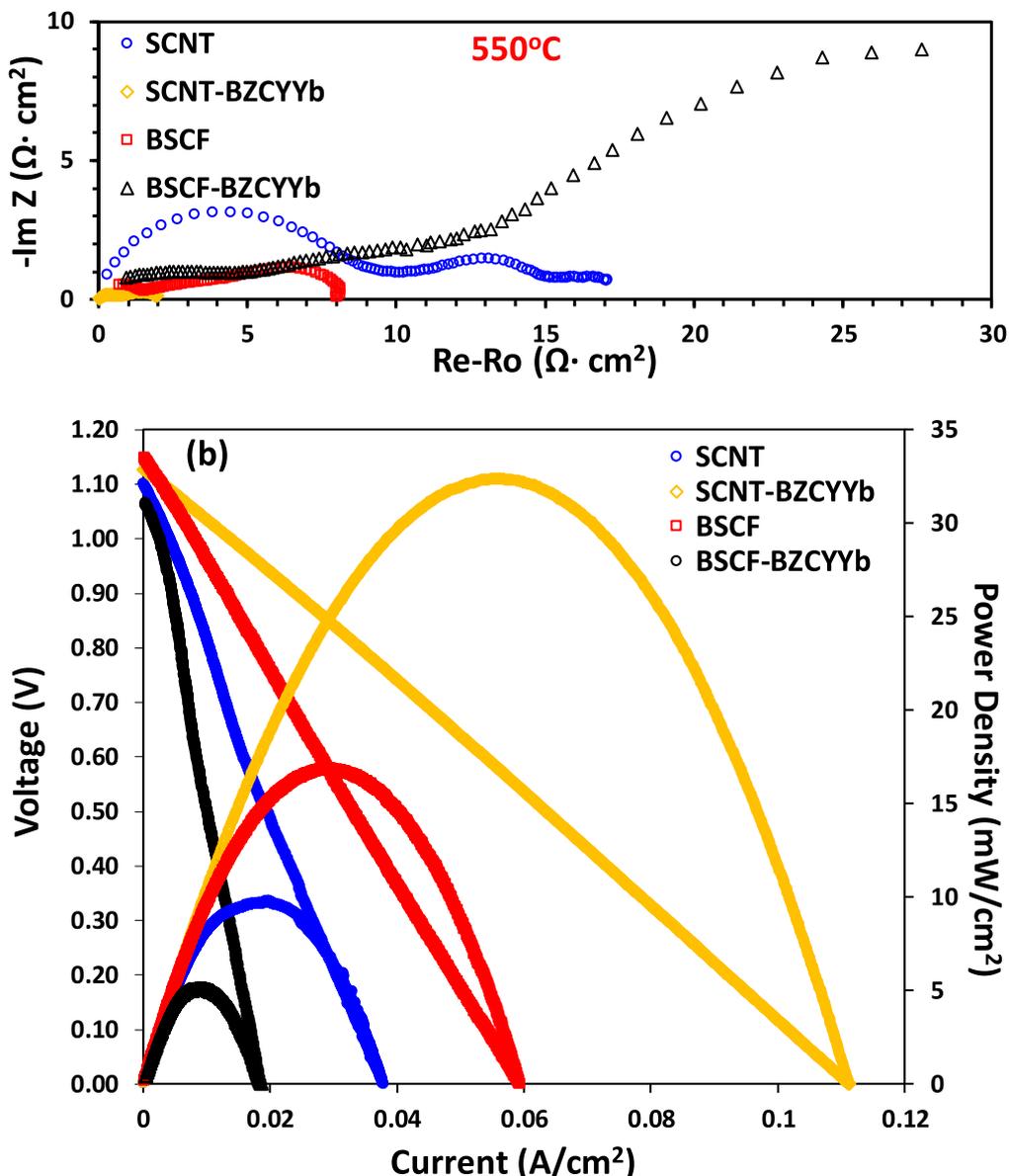
**Figure 5.** Impedance spectra under open circuit condition (a) and  $j - V/j - p$  curves (b) for BZCYYb electrolyte-supported PC-SOFC button cell with different cathodes of pure SCNT, SCNT-BZCYYb composite, pure BSCF, and BSCF-BZCYYb composite at 650 °C.

PC-SOFC button cells indicates that at an intermediate temperature, the difference in cell  $R_p$  comes primarily from the high frequency (HF, in the range of  $\sim 10^6$  to  $10^4$  Hz) resistance  $R_{HF}$ : pure SCNT cathode gives  $R_{HF}$  several times larger than pure BSCF cathode, as shown in Fig. 8b, while the mid-to-low frequency (MF-LF, in the range of  $\sim 10^4$  to  $10^{-2}$  Hz) resistance  $R_{MF-LF}$  are comparable, as

shown in Fig. 8c. (Note here, the  $R_{HF}$  and  $R_{MF-LF}$  values are extracted directly from the EIS curves as the width (along real axis) of the high frequency loop in the range of  $\sim 10^6$  to  $10^4$  Hz and the mid-to-low frequency loop(s) in the range of  $\sim 10^4$  to  $10^{-2}$  Hz, respectively. The two together make up for the total polarization resistance  $R_p$ . See<sup>13,18</sup> for more details.)

**Table I. Elementary steps (and their reverse steps) of the cathode oxygen reduction reaction (ORR) for a conventional OC-SOFC (step 1, 2, 3, 4) vs an ideal PC-SOFC (step 1, 2, 3', 4', 5').**<sup>13,17,18,21</sup>

#	Elementary step	Frequency range in EIS (Hz)	Hypothetical Reaction
1	Oxygen adsorption	LF ( $\sim 10^0 - 10^{-2}$ )	$O_2(g) \leftrightarrow O_2(ads)$
2	Oxygen dissociation	MF ( $\sim 10^4 - 10^0$ )	$O_2(ads) \leftrightarrow 2O(ads)$
3	Charge transfer (oxide-ion)	HF ( $\sim 10^6 - 10^4$ )	$O(ads) + V_{O}^{\bullet\bullet} + 2e^- \leftrightarrow O_O^X$
3'	Charge transfer (proton)	HF ( $\sim 10^6 - 10^4$ )	$O(ads) + 2e^- + 2OH_{O}^{\bullet\bullet} \leftrightarrow H_2O(ads) + 2O_O^X$
4	Mass transfer (oxide-ion)	Very HF ( $\gg 10^6$ )	$V_{O(electrode)}^{\bullet\bullet} \leftrightarrow V_{O(electrolyte)}^{\bullet\bullet}$
4'	Mass transfer (proton)	Very HF ( $\gg 10^6$ )	$OH_{O(electrode)}^{\bullet} \leftrightarrow OH_{O(electrolyte)}^{\bullet}$
5'	H <sub>2</sub> O transport and desorption	LF ( $\sim 10^0 - 10^{-2}$ )	$H_2O(ads) \leftrightarrow H_2O(g)$



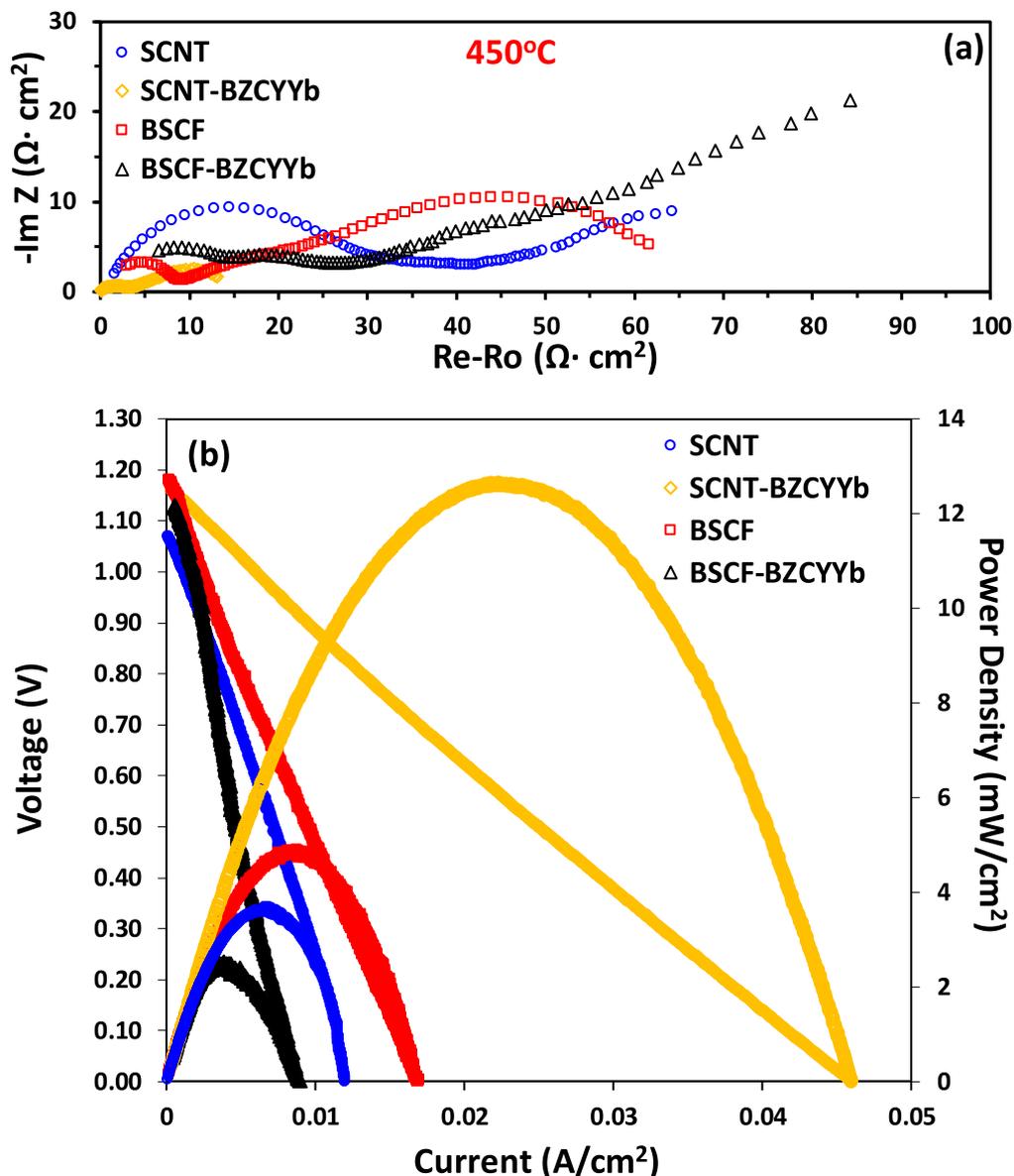
**Figure 6.** Impedance spectra under open circuit condition (a) and  $j - V/j - p$  curves (b) for BZCYYb electrolyte-supported PC-SOFC button cell with different cathodes of pure SCNT, SCNT-BZCYYb composite, pure BSCF, and BSCF-BZCYYb composite at 550 °C.

The observation above (i.e., much larger  $R_{\text{HF}}$  for pure SCNT than pure BSCF cathode) seems to suggest slower charge transfer for the pure SCNT cathode than pure BSCF cathode for current electrolyte-supported PC-SOFC since the HF process is generally associated with charge transfer (dominated by the cathode process for the two-electrode button cell in this case).<sup>17</sup> However, whether this means the underlying charge transfer process over pure SCNT is *intrinsically* slower than pure BSCF for a PC-SOFC still needs to be studied further because the two cathodes' microstructures (e.g., active surface area and three-phase-boundary (TPB) length) are not exactly the same. Nevertheless, this is different from the situation when the two materials are used as cathodes for OC-SOFC: As stated before, pure SCNT cathode gives maximum power of  $\sim 0.7 \text{ W cm}^{-2}$  on anode-supported OC-SOFC at 450 °C,<sup>20</sup> while pure BSCF cathode only gives maximum power of  $\sim 0.2\text{--}0.3 \text{ W cm}^{-2}$  (both with  $\sim 14 \mu\text{m}$  thick  $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$  or GDC electrolyte).<sup>19</sup>

That pure SCNT *underperforms* pure BSCF when used as a practical porous cathode for PC-SOFC at *intermediate temperature* is understood as follows. As stated, at an intermediate temperature such as 550 °C, the BZCYYb electrolyte should predominantly

demonstrate proton conductivity under humidified condition or in a hydrogen-air fuel cell,<sup>25,27</sup> and the ORR charge transfer step should follow the proton-based route as in step (3'). If the cathode material conducts not only electron hole but also proton, the entire cathode surface would be active for ORR, leading to fast cathodic reaction and high performance (i.e., low  $R_p$  and high  $P_{\text{max}}$ ). This is believed to be the case for pure BSCF cathode for PC-SOFC<sup>13,17,28</sup> since earlier study by Grimaud shows that BSCF powder has significant water uptake of up to  $\sim 0.8 \text{ wt}\%$  after the water saturation treatment (see also Fig. 3), corresponding to a moisture content of  $\sim 10 \text{ mol}\%$  at 450 °C in the BSCF material.<sup>17</sup> The absorbed water molecules would interact with oxygen vacancies in BSCF to form protons, leading to mixed protonic and electronic conduction in BSCF and reasonably fast reaction rate for cathode ORR of PC-SOFC since proton could travel from the BZCYYb electrolyte to BSCF, of which the entire surface would be active for the cathode reaction.

In comparison, SCNT is more like LSCF and does not contain the strongly-basic barium ion ( $\text{Ba}^{2+}$ ). As a result, SCNT should not have too great affinity for moisture, which is confirmed by the TGA for pre-hydrated SCNT powder: As shown before in Fig. 3, SCNT



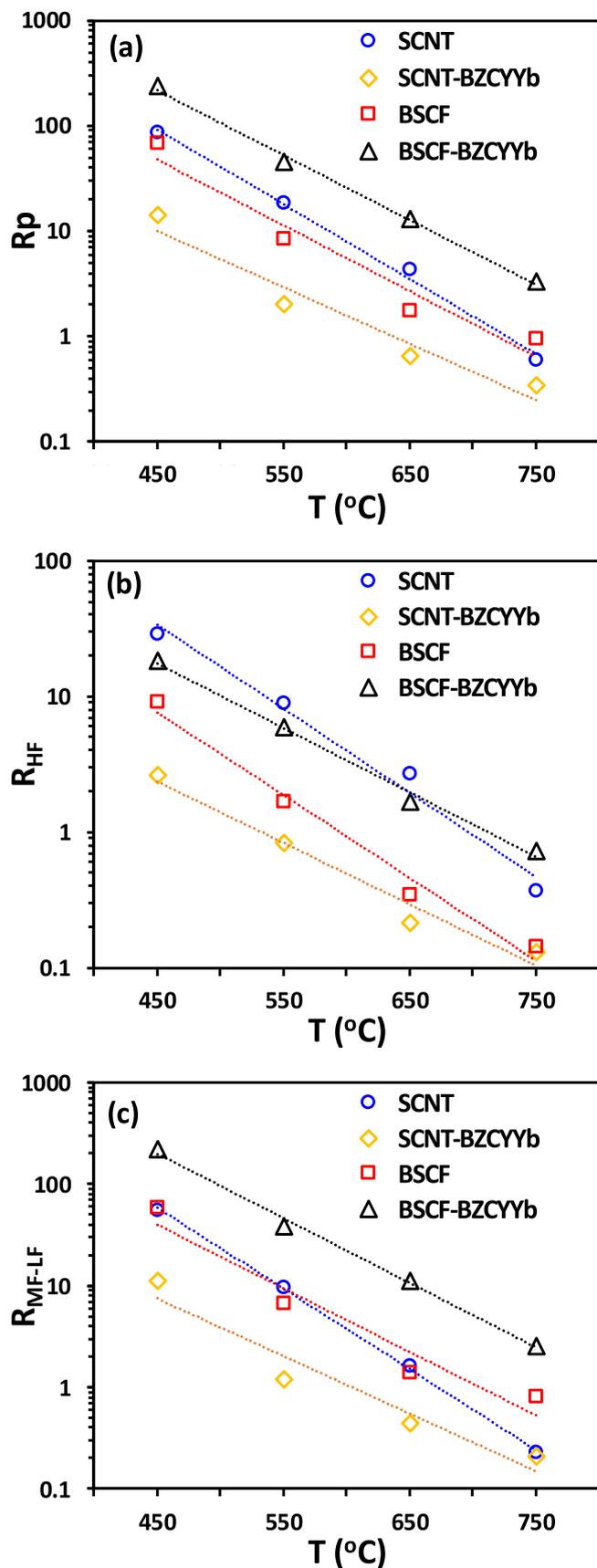
**Figure 7.** Impedance spectra under open circuit condition (a) and  $j - V/j - p$  curves (b) for BZCYYb electrolyte-supported PC-SOFC button cell with different cathodes of pure SCNT, SCNT-BZCYYb composite, pure BSCF, and BSCF-BZCYYb composite at 450 °C.

displays negligible difference in sample weight between the heating and the cooling processes, corresponding to a low water content of  $< \sim 0.1$  wt% despite the water saturation treatment. The implication is that SCNT would not readily absorb/retain moisture to form protons and transport them. Thus, for the *pure* SCNT cathode in PC-SOFC, the reaction sites for step (3') charge transfer in cathode ORR would be strictly limited to the air-BZCYYb proton conducting electrolyte-SCNT cathode TPB at the planar cathode-electrolyte interface, which does not offer as many reaction sites. As a result, it is not surprising that at intermediate temperature, *pure* SCNT underperforms pure BSCF as the cathode for PC-SOFC.

Note that the above explanation for why pure SCNT underperforms pure BSCF as cathode for PC-SOFC at intermediate temperature is supported by two additional observations. First, SCNT has much higher electronic (and also total electric) conductivity than BSCF: For example, at 550 °C, literature report SCNT total electric conductivity to be  $\sim 70$ – $130$   $\text{s cm}^{-1}$ ,<sup>20,29</sup> while Li et al., reports BSCF total electric conductivity to be  $\sim 30$   $\text{s cm}^{-1}$ .<sup>30</sup> This means the cathode reaction over SCNT is unlikely to be limited by electronic or total electric conductivity. In addition, pure SCNT, which has the

nominal formula of  $\text{SrCo}_{0.8}\text{Nb}_{0.1}\text{Ta}_{0.1}\text{O}_{3-\delta}$ , does contain significant concentration of oxygen vacancy, which is evidenced by the clear weight loss when it is heated up to in dry air, as shown before in Fig. 3. For example, when it is heated to 1000 °C, the weight loss is  $\sim 1.0$  wt% and the estimated oxygen deficiency  $\delta \approx 0.4$  (or  $\sim 13\%$  of lattice oxygen is lost); while when heated to 550 °C, weight loss is  $\sim 0.2$  wt% and the estimated oxygen deficiency  $\delta \approx 0.08$  (or  $\sim 2.6\%$  of lattice oxygen is lost). Recent study has also shown SCNT to be very active towards oxygen surface adsorption and exchange,<sup>29</sup> which means the cathode reaction over pure SCNT is unlikely to be limited by oxygen adsorption/exchange.

On the other hand, it is noted that when the operating temperature is raised to 750 °C, pure SCNT seems to catch up to BSCF as the cathode for PC-SOFC. As shown in Fig. 4 and Fig. 8, the cell power and total  $R_p$  are comparable for the two cathodes at 750 °C: BSCF cathode still offers much lower  $R_{\text{HF}}$  than SCNT, yet  $R_{\text{MF-LF}}$  becomes much higher for BSCF. One possible explanation is that although the mixed protonic and electronic conducting BSCF enables faster charge transfer than SCNT (see Fig. 8b), the high temperature of 750 °C means BSCF surface would have difficulty holding onto



**Figure 8.** Plots of (a) total cell polarization resistance  $R_p$ , (b) high frequency loop resistance  $R_{HF}$ , and (c) mid-to-low frequency loop (s) resistance  $R_{MF-LF}$  vs temperature for BZCYyb electrolyte-supported PC-SOFC button cells with different cathodes including pure SCNT, SCNT-BZCYyb composite, pure BSCF, BSCF-BZCYyb composite from 750 °C to 450 °C. The anodes for all cells remain the same of Ni-BZCYyb cermet.

water molecules and forming protons: (In fact, according to Grimaud, the water content in BSCF at 750 °C is only a quarter of that at 450 °C.<sup>17</sup>) The slower water adsorption/hydration for BSCF are expected to show up as the larger mid-to-low frequency loop in EIS, as seen in Fig. 4a and Fig. 8c. Overall, the performance in PC-SOFC appear comparable for pure SCNT vs pure BSCF at 750 °C.

**SCNT-BZCYyb composite cathode for PC-SOFC and the impact of water affinity on BSCF-based cathodes.**—Although pure SCNT does not appear to be a very effective cathode for BZCYyb electrolyte-supported PC-SOFC at intermediate temperature (~450 °C–650 °C), with the addition of BZCYyb to make a SCNT-BZCYyb composite cathode, the performance for the BZCYyb electrolyte-supported PC-SOFC button cells improves dramatically, as shown in Figs. 5 to 7 and Fig. 8. The overall interfacial resistance  $R_p$  under open circuit condition drops by ~80%–90%, while the maximum power density increases by ~100%–300% as compared with the pure SCNT cathode! Such a large improvement upon introduction of the BZCYyb electrolyte phase into the cathode for PC-SOFC is not difficult to understand.

As discussed before for Fig. 3, SCNT does not show much affinity for water uptake. Therefore, it would not be a good (mixed) protonic conductor. A pure SCNT cathode for an intermediate temperature PC-SOFC means all cathodic reaction would be confined to the flat cathode-electrolyte interface, which offers rather limited reaction sites. As a result, the cathode reaction would be slow, which is observed in the experiments. Although pure SCNT still has significant oxygen vacancy in air (see discussion near the end of previous section), it is not regarded to be too helpful because the cathode ORR for such PC-SOFC at intermediate temperature is primarily based on proton (reaction i) instead of oxide ion (or oxygen vacancy).

When adding the proton conducting BZCYyb electrolyte phase to make a SCNT-BZCYyb composite cathode, the number of air-proton conducting electrolyte (in this case, BZCYyb)-electronic conducting phase (in this case SCNT) TPB reaction sites naturally increase dramatically, leading to much higher cathode reaction rate and better overall cell performance, as observed in the experiments. Meanwhile, the electronic conduction of BZCYyb electrolyte is unlikely to play any significant role here due to the high electric conductivity of SCNT itself<sup>20,29</sup> and the low electronic transference number of BZCYyb at intermediate temperature, especially in humidified air.<sup>25</sup>

It is also interesting to note that the SCNT-BZCYyb composite cathode appears even more active than the pure BSCF cathode at 450–650 °C, as shown in Figs. 5–7 and Fig. 8, despite that BSCF readily absorbs moisture and would conduct both proton and electron holes, which enables the entire surface of BSCF to be active for the cathode reaction. By contrast, adding BZCYyb to BSCF to make a BSCF-BZCYyb composite cathode actually makes the PC-SOFC performance worse by giving much larger  $R_p$  and significantly reduced maximum power output.

Although whether the later observation (i.e., BSCF-BZCYyb composite underperforms pure BSCF as PC-SOFC cathode) is due to reduced effective electric conductivity (as a result of BZCYyb disrupting the current pathway through BSCF) or some other factors (e.g., overly strong water adsorption) is not clear, it at least suggests adequate proton conductivity for the pure BSCF cathode.

Meanwhile, the implication from the former observation (SCNT-BZCYyb composite outperforms pure BSCF as cathode for PC-SOFC) is that a single phase mixed protonic and electronic conductor (e.g., BSCF here) might not be the optimal choice for PC-SOFC. This may be attributed to BSCF's (overly) strong affinity for H<sub>2</sub>O at intermediate temperature (e.g., up to ~10 mol% of water uptake at ~450 °C, according to Grimaud<sup>17</sup>), which is required for adequate proton formation and conduction but might actually interfere with the oxygen adsorption and dissociation steps (step 1 and 2) on BSCF surface. In fact, our earlier study has shown that for

pure BSCF cathode over BZCYYb electrolyte, the overall cathode interfacial resistance increases by more than 100% when the atmosphere is switched from relatively dry air (moisture content  $\ll 1\%$ ) to 3 vol% humidified air.<sup>18</sup> BSCF's much stronger affinity for moisture (and maybe CO<sub>2</sub> as well!) than SCNT might also be a factor in explaining literature results showing pure BSCF greatly underperforms pure SCNT at  $\sim 450^\circ\text{C}$  when the two were compared as cathode for OC-SOFC with ceria-based electrolyte, despite they display similar weight loss (both  $\sim 1.0\text{ wt}\%$ , after correcting for hysteresis from moisture absorption, which can be a direct indication of oxygen vacancy concentration in these cathode materials) during TGA in dry air. (Note that literature as well as authors' earlier studies have shown BSCF maintains its bulk phase stability upon heat treatments in air containing moisture, but the surface adsorption of moisture (and CO<sub>2</sub>) over BSCF is expected to be strong.<sup>18,19,29</sup>

Finally, from the current study, it seems that instead of trying to use a single phase cathode material to resolve the conflict between the need for water affinity for proton formation and conduction and the need for active oxygen adsorption/dissociation (both required for the cathode of intermediate temperature PC-SOFC), the composite cathode approach such as the SCNT-BZCYYb composite used here might be more versatile and better fitted to achieve higher performance: One phase—the BZCYYb proton conducting electrolyte phase could provide the desired water absorption and resulting proton conduction, while the other phase of SCNT with its high oxygen vacancy concentration and surface exchange rate<sup>20,29</sup> but low water affinity could provide the required high electronic conductivity and fast oxygen surface exchange. Of course, the cathode reaction would occur at the TPB sites in this case, but there should be plenty of room to optimize the relative amount and microstructure and adopt additional strategy (e.g., function/composition gradient or infiltration) to maximize TPB length and enhance the performance of such composite cathode for intermediate temperature PC-SOFC.

### Conclusions

In summary, a leading mixed oxide-ionic and electronic conducting cathode for intermediate temperature oxide-ion conducting SOFC, SrCo<sub>0.8</sub>Nb<sub>0.1</sub>Ta<sub>0.1</sub>O<sub>3- $\delta$</sub>  (SCNT), is evaluated as the cathode for proton conducting SOFC (PC-SOFC) using BZCYYb proton conducting electrolyte-supported button cells. The cathode is also compared with BSCF, which has significant water uptake capability in humidified air and demonstrates mixed protonic and electronic conduction. It was observed that pure SCNT does *not* perform as well as pure BSCF as the cathode for the BZCYYb electrolyte-supported PC-SOFC at intermediate temperatures (e.g.,  $\sim 650^\circ\text{C}$ – $450^\circ\text{C}$ ). This is attributed to the observed low water uptake for SCNT, which indicates limited proton formation and confinement of the cathode reaction to the cathode-electrolyte interface with limited sites. In comparison, the strong water absorption and resulting mixed protonic and electronic conduction for BSCF enables all BSCF cathode surface to be active, leading to faster cathode reaction at intermediate temperature.

On the other hand, mixing SCNT with BZCYYb to form a composite cathode for PC-SOFC improves the performance dramatically. This is attributed to the extended TPB area in the SCNT-BZCYYb composite cathode. The observation that such SCNT-BZCYYb composite even outperforms pure BSCF as cathode for

PC-SOFC suggests that a single phase mixed protonic and electronic conducting cathode material with strong hydration such as BSCF might not be optimal for PC-SOFC: The BSCF's strong affinity for water, though desirable for proton formation, seems to interfere with oxygen adsorption and dissociation and limit cathode reaction rate. In comparison, a composite cathode such as SCNT-BZCYYb seems to enable better balance between the need for water absorption and proton conduction and the need for oxygen adsorption/exchange and could be more suitable for PC-SOFC operating at intermediate temperature, especially at or below  $550^\circ\text{C}$ . Future study using similar materials but on state-of-the-art anode supported PC-SOFC will be carried out to confirm the observations made here based on electrolyte-supported cells and also provide further understandings.

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