Nanostructured Carbon Electrocatalyst Supports for Intermediate-Temperature Fuel Cells: Single-Walled Versus Multi-Walled Structures

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Abstract

It is unknown if nanostructured carbons possess the requisite electrochemical stability to be used as catalyst supports in the cathode of intermediate-temperature solid acid fuel cells (SAFCs) based on the CsH_2PO_4 electrolyte. To investigate this application, single-walled carbon nanohorns (SWNHs) and multi-walled carbon nanotubes (MWNTs) were used as supports for Pt catalysts in SAFCs operating at 250 °C. SWNH-based cathodes display greater maximum activity than their MWNT-based counterparts at a cell voltage of 0.8 V, but are unstable in the SAFC cathode as a consequence of electrochemical carbon corrosion. MWNT-based cells are resistant to this effect and capable of operation for at least 160 hours at 0.6 V and 250 °C. Cells fabricated with nanostructured carbon supports are more active (52 mA cm^{-1} *vs.* 28 mA cm^{-1} at 0.8 V) than state-of-the-art carbon-free formulations while simultaneously displaying enhanced Pt utilization ($40 \text{ mA mg}_{\text{Pt}}^{-1}$ *vs.* $16 \text{ mA mg}_{\text{Pt}}^{-1}$ at 0.8 V). These results suggest that MWNTs are a viable support material for developing stable, high-performance, low-cost air electrodes for solid-state electrochemical

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devices operating above 230 °C.

Keywords: CsH₂PO₄, carbon nanotubes, carbon nanohorns, fuel cells

1. Introduction

Fuel cells based on the crystalline solid acid proton conductor CsH₂PO₄[1] (CDP), hereafter termed solid acid fuel cells[2, 3] (SAFCs) are a relatively new class of devices with the potential for adoption in stationary applications. SAFCs operate at approximately 250 °C, an intermediate temperature regime that eliminates the need for management of liquid reaction products or liquid electrolytes, while preserving access to a conventional materials set for components. Intermediate-temperature operation also confers an excellent resistance to poisoning on Pt[3], Pd[4], and Ru[5] anode catalysts, permitting the use of minimally processed reformed hydrocarbon fuels.

In contrast with the robust attributes of the anode, the current state of the cathode limits the potential reach of SAFCs. **SAFCs are entirely solid state systems and do not benefit from either an oxygen-permeable ionomer or the presence of liquid water, attributes conducive to high catalyst utilization in low-temperature polymer-based systems. A low active surface area in CDP-based systems impacts cathode performance strongly[1, 3]. In response to this problem,** the state-of-the-art SAFC cathode is based on a macroporous framework of the CDP electrolyte conformally coated by a network of Pt nanoparticles that serves as both the oxygen reduction catalyst and the electronic conductor[6, 7], **to maximize catalyst-electrolyte interfacial area.** This architecture is limited by the critical quantity of Pt required to maintain a percolating electronic conduction network in the electrode, resulting in undesirably high Pt loadings ($> 1.5 \text{ mg}_{Pt} \text{ cm}^{-2}$)[6].

Implementation of durable electronically-conductive additives may be a pathway to lowering SAFC cathode Pt loadings to competitive levels. This is certainly the dominant approach in low-temperature polymer systems and the intermediate-temperature phosphoric acid system, both of which rely on car-

bon as a catalyst support[8]. These systems have typically used turbostratically disordered carbons found on the continuum between completely amorphous carbon black and perfectly ordered graphite, balancing the high surface area and porosity of the former with the electrochemical stability of the latter.

Electrochemical stability is a critical parameter in a fuel cell electrode, as carbon can itself react with water (a reaction product), either forming surface oxide species or carbon dioxide according to the carbon corrosion[9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19] reaction

resulting in degradation of the electrode as carbon is lost in the gas phase.

Nanostructured carbons have been examined for some time as potential substituents in fuel cell electrodes due in part to their ability to resist this process of carbon corrosion. Substantial progress has been made in implementing metallic catalysts supported on multiwalled carbon nanotubes[20, 21, 22, 23, 24, 25], single-walled carbon nanotubes[21, 22, 24, 26, 25], and single-walled carbon nanohorns[21, 25, 27, 28, 29, 30] in low-temperature acidic environments and in the intermediate-temperature phosphoric acid systems.

Previous work focused on implementing nanostructured carbon in SAFCs demonstrated novel architectures[31, 32, 33] with ultra-low Pt loadings applied to the H_2/H^+ redox couple at the anode. It remains an open question if carbon is a viable support material at the higher electrochemical potentials of the cathode. In this contribution, we address that question, investigating the use of both single-walled and multi-walled carbon nanostructures, in the form of nanohorns (SWNHs) and nanotubes (MWNTs), respectively, as catalyst supports in the SAFC cathode.

2. Experimental Methods

2.1. Materials Preparation

SWNHs were prepared via a laser vaporization procedure very similar to that described previously[34, 35, 36]. Carbon targets were prepared from a

graphite adhesive (BC628, Bay Composites). The adhesive was initially baked in a closed vessel at 120 °C for 4 hours. The resulting target was then annealed at 800 °C under flowing Ar for 4 hours to remove any residual solvents. Pulsed laser vaporization (PLV) of the SWNHs was completed in a quartz tube reactor at 1100 °C in 735 torr and 2L min⁻¹ of Ar flow. A Nd:YAG ($\lambda = 1.064 \mu\text{m}$) laser with typical pulse power of 420 W was used to ablate the targets and the resulting products were collected in a HEPA-filtered collection chamber.

Commercial MWNTs (Cheaptubes) were used as received.

Pt catalysts supported on SWNHs and MWNTs were synthesized from Pt(II)-pentanedionate precursor (Strem) in a fixed bed at 210 °C under a reduced pressure N₂-H₂O atmosphere. **In this procedure the solid Pt precursor is intermixed with the solid support and heated slowly in a deoxygenated atmosphere, causing sublimation, adsorption, and finally decomposition of the precursor to zero-valent Pt. This route is similar to other supported metallic catalyst syntheses that we have reported[4, 7, 6, 37, 5].**

2.2. Materials Characterization

Pristine and post-test 60 wt%Pt/SWNH and 60 wt%Pt/MWNT were characterized by high-resolution transmission electron microscopy (HRTEM) imaging in a Zeiss Libra 200 MC TEM at an acceleration voltage of 200 kV. The information limit of HRTEM images in this microscope is ~ 0.1 nm. Imaging of SAFC cathodes in cross-section was performed with a Zeiss Auriga 40 SEM at an accelerating voltage of 3 kV using the in-lens detector with a resolution of approximately 2-3 nm.

Powder X-ray diffraction patterns were recorded with a Bruker D2 Phaser diffractometer with Ni-filtered Cu K α radiation ($\lambda = 0.15418$ nm). Raman spectra were recorded by a Renishaw 1000 confocal microRaman spectrometer with an excitation wavelength of 532 nm under a 50 $\times$ objective and 10% laser power.

84 2.3. Cell Fabrication

85 Solid acid fuel cells were fabricated using an anode-supported configuration
86 similar to those described previously[3, 6, 7]. Using a bilayer sintered stainless
87 steel (grade 304) mesh disc (2.85 cm^2) as an anode current collector and struc-
88 tural support, anode, membrane, and cathode layers were sequentially formed
89 by uniaxial compression of powdered composites in a stainless steel die. An-
90 odes were formed at $\sim 90 \text{ MPa}$ from a mechanical mixture of CDP, 60wt%Pt
91 supported on carbon black (Vulcan XC-72R, Cabot Corp.) and naphthalene (a
92 fugitive binder) in a 3:1:1 ratio, respectively, by weight. The CDP membrane
93 was applied to the anode at 125 MPa and was approximately $50 \text{ }\mu\text{m}$ in thick-
94 ness. Experimental cathodes comprised of 25 mg of a 3:1 by weight mixture of
95 CDP and 60wt%Pt supported on either MWNTs or SWNHs were applied to
96 the dense CDP membrane at a pressure of 30 MPa . The areal Pt loading of
97 the experimental cathodes was $1.3 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$, and each contained 0.88 mg of
98 carbon per cm^{-2} . State-of-the art cathodes were comprised of 25 mg of 20 wt%
99 Pt supported on fine CDP[6] laminated at 30 MPa with a Pt loading of 1.75
100 $\text{mg}_{\text{Pt}} \text{ cm}^{-2}$. Cathode current collectors were coarse single-layer stainless steel
101 (grade 316) mesh and a carbon paper interlayer (SGL 34AA).

102 2.4. Electrochemical Testing

103 Fuel cell testing was conducted using stainless steel test rigs at a temper-
104 ature of $250 \text{ }^\circ\text{C}$ with gases hydrated to a dew point of $75 \text{ }^\circ\text{C}$ (approximately
105 0.35 bar water partial pressure). Anodes were supplied ultrahigh-purity H_2 at
106 a flow rate of 30 sccm and cathodes were supplied compressed air flowing at
107 70 sccm , provided by a centralized compressor. No back pressure was applied
108 to either fuel or oxidant exhaust streams. Polarization curves were recorded
109 with a Bio-Logic VSP potentiostat by scanning the working electrode potential
110 at 10 mV s^{-1} from the open circuit potential to a cell potential of 0 V . Each
111 cell was subjected to a multi-step cyclic testing protocol consisting of 1.) a 10-
112 second relaxation to the open circuit voltage 2.) recording of a potentiostatic
113 electrochemical impedance spectroscopy (EIS) spectrum from 200 kHz to 200

114 mHz at 0.8 V cell voltage with single sine perturbation amplitude of 10 mV 3.)
 115 recording of the polarization curve 4.) EIS spectrum 5.) 30 minute potentio-
 116 static hold at 0.6 V, followed by a repetition of this protocol. After 30 cycles the
 117 cells were held at 0.6 V. The high-frequency intercept of the EIS spectrum was
 118 used to eliminate the ohmic resistance of the cell from the polarization curves,
 119 yielding what we refer to as iR-free polarization curves. Multiple cells were con-
 120 structed for each electrode formulation, and plots of iR-free polarization curves
 121 (Figure 5b), HFR, and current density at 0.6 V (Figure 6) are averaged across
 122 these cells.

123 Corrosion testing was performed a temperature of 250 °C with gases hy-
 124 drated to a dew point of 75 °C. Anodes were supplied ultrahigh-purity H₂ and
 125 cathodes were supplied ultrahigh-purity N₂. Corrosion currents were acquired
 126 via chronoamperometry at 1.0 V cell potential for 1800 s.

127 3. Results and Discussion

128 Platinum nanoparticles (60 wt%) were deposited on single-walled carbon
 129 nanohorns (SWNH) and multiwalled carbon nanotubes (MWNT) using a va-
 130 por deposition procedure[4, 5, 6, 7, 37]. High-resolution transmission electron
 131 microscopy (HRTEM) images of the SWNHs (see Supplementary Information)
 132 reveal a structure consisting of individual cone-shaped nanohorns with walls
 133 consisting of a single graphene layer and diameters of approximately 2 nm and
 134 lengths of approximately 10 nm, clustered into a secondary dahlia-like aggre-
 135 gate structure. HRTEM images of pristine MWNTs show structures 10-20 nm
 136 in diameter with walls comprised of 10-20 graphene layers, closed ends, and in-
 137 ternal herringbone nanostructure. MWNTs also contained approximately 1wt%
 138 encapsulated Co remnant from CVD synthesis.

139 The XRD profile of as-synthesized SWNHs (Figure 1a) reveals two sharp
 140 diffraction peaks as well as broader features. We note a sharp peak at 26.4° cor-
 141 responding to the graphitic (002) plane[38], in addition to a peak at 25.9° which
 142 may be attributed to diffraction from adjacent SWNH walls. An asymmetric

Figure 1: Cu K α x-ray diffraction patterns for pristine carbon supports and supports decorated with 60 wt% Pt.

143 diffraction peak observed at $2\theta \sim 43.3^\circ$ is assigned to the (100) reflection[39, 38].
 144 The breadth and asymmetry of this peak originate from a lack of long-range
 145 correlations apart from those within the two-dimensional graphene sheets com-
 146 prising the SWNH walls. XRD analysis of the as-received MWNTs is consistent
 147 with typically observed MWNT diffraction patterns, including a characteristi-
 148 cally strong (002) graphite peak.

149 HRTEM (Figure 2) images of the Pt-decorated composites show Pt particles
 150 with adequate dispersion in a range from 3-5 nm in diameter, with mean particle
 151 sizes of 3.6 nm for 60 wt%Pt/SWNH and 3.3 nm for 60 wt%Pt/MWNT. This
 152 is in agreement with Scherrer analysis of x-ray diffraction patterns (Figure 1b)
 153 which returns coherence lengths of 2.8 nm for 60 wt%Pt/SWNH and 3.2 nm for
 154 60 wt%Pt/MWNT. No Pt particles were judged to be on the interior surfaces
 155 of the supports based on TEM observation.

Figure 2: (HRTEM images of 60 wt% Pt on SWNHs (left panels) and on MWNTs (right panels).

156 Raman scattering measurements of as-synthesized SWNHs (Figure 3 are
 157 consistent with other reports[36, 40]. Using the ratio of **D-band ($\sim 1350 \text{ cm}^{-1}$)**
 158 **to G-band ($\sim 1600 \text{ cm}^{-1}$)** intensity as a measure of structural disorder, we find
 159 a ratio slightly greater than 1 for the SWNHs and 0.75 for MWNTs, indicating
 160 greater defect density in the SWNH sample. We observe a slight blue shift
 161 of the SWNH G-band upon Pt deposition (approximately 8 cm^{-1}), possibly
 162 attributable to decreased electron density in the C=C bonds[41]. This effect is
 163 not present in the case of 60 wt%Pt/MWNT. However in both cases we note
 164 a slight decrease in the intensity of the G' band, a sensitive indicator of long-
 165 range order[42] that unsurprisingly is disrupted by introduction of a high metal
 166 loading of Pt in via chemical vapor treatment.

167 SAFC cathodes ($1.3 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$) formed from 3:1 (by weight) mixtures of the

Figure 3: Raman spectra for pristine carbon supports and supports decorated with 60 wt% Pt.

168 60 wt%Pt/C and CDP are shown in Figure 4. The cathode based on SWNHs
 169 is approximately 35 μm in thickness while the MWNT-based cathode is slightly
 170 thicker, $\sim 45 \mu\text{m}$. We note also that the SWNH sample appears to be qualita-
 171 tively more homogeneous than the MWNT sample.

172 Fuel cell polarization curves for the experimental electrodes are shown in
 173 Figure 5. We note a substantially higher open circuit voltage (OCV) in the case
 174 of the MWNT electrode in comparison with the SWNH electrode (0.97 V vs.
 175 0.93 V, respectively), which we attribute to a mixed potential arising from the

Figure 4: FESEM micrographs of as-fabricated SWNH-based (left panels) and MWNT-based (right panels) SAFC electrodes.

176 carbon corrosion reaction (Equation 1) investigated in more depth below. At
 177 an arbitrary voltage of 0.8 V (selected to be representative of electrode kinet-
 178 ics) the SWNH electrode is approximately 15% more active than the MWNT
 179 electrode. At the higher currents, the MWNT cell maintains a higher voltage, a
 180 consequence of its relatively lower ohmic resistance ($0.27 \Omega \text{ cm}^2$ for the MWNT
 181 cell vs. $0.35 \Omega \text{ cm}^2$ for the SWNH cell). The consequences of this disparity
 182 are also evident in the iR -free representation (Figure 5b), whereupon removal
 183 of the ohmic contribution the activity of the SWNH cell is very close to that
 184 of the MWNT cell across the entire current range. The lower resistance of the
 185 MWNT cell results in a 21% increase in maximum power density with respect
 186 to the SWNH cell (246 mW cm^{-2} versus 202 mW cm^{-2} , respectively; see Sup-
 187 plementary Information). These initial differences in ohmic resistance could

originate from the incipient effects of carbon corrosion, which we investigate in more detail below.

Figure 5: (a) Uncorrected and (b) average iR-free SAFC polarization curves recorded at 250 °C with H₂/air at 75 °C dew point for SWNH-based or MWNT-based cathodes. Insets show enlargement of the kinetic region.

Also clear in the iR-free data of Figure 5b is a deviation of the two corrected polarization curves at the extreme end of the current range. The MWNT cell displays a signature of mass-transport limited behavior in the negative convexity of the iR-free polarization curve at high current, while this is absent in the case of the SWNH cell. This may be a consequence of differences in the mixing of the electrolyte with the electrocatalyst, as we observed via SEM (Figure 4). The reduced thickness of the SWNH cathode could also result in more facile transport, though more detailed studies of reactant transport are required to validate this speculation.

We observed substantial and disparate changes in the polarization curves of the single-walled and multi-walled supports over the course of 20 hours of cyclic testing (Figure 6). Two effects are clear: a gradual increase in the performance of the MWNT cell, and a brief increase followed by a precipitous decline in the performance of the SWNH cell that is correlated with a large increase in its

Figure 6: (a) Average high-frequency resistance (HFR) and (b) average current density at 0.6 V cell voltage for experimental SAFC cathodes recorded at 250 °C with H_2 /air hydrated to 75 °C dew point. Triangular markers indicate the testing cycles selected for Figure 5

cell ohmic resistance (HFR). The observed HFR increase is likely to be caused by loss of carbon from the electrode, increasing interfacial contact resistance, a phenomenon that has also been observed in the case of PEMFCs[43, 44, 45]. Additionally, in the case of the experimental SAFCs cathodes, the carbon volume fraction is relatively low, and regions close to the CDP membrane could become completely devoid of percolating electronically-conductive domains via corrosion. This would effectively increase the spatial extent of the ionic conductor and increase the ohmic resistance of the cell. Furthermore, loss of carbon proximate to the Pt catalyst could result in physical detachment of the catalyst from the electronic transport network, again effectively reducing the electrochemically active surface area in the electrode. In the case of the SWNH cell, the inverse correlation of current density and HFR here is not surprising, given

216 the impact of ohmic losses of the polarization curve at higher cell currents.
217 **Based on these results** we conjectured that carbon corrosion was dominant in
218 the loss of performance of the SWNH cell.

219 To test this hypothesis, we subjected fresh experimental cathodes at their
220 peak performance to an accelerated corrosion test, holding the cell potential at
221 1.0 V with the cathode in a humidified inert atmosphere (N_2 at 75 °C dew point)
222 with the anode under standard conditions (H_2 at 75 °C dew point). Voltage
223 has been explored previously as an accelerant of the carbon corrosion reaction
224 in both phosphoric acid[9, 10, 11, 12, 13] and polymer-electrolyte[14, 46, 22, 19]
225 environments. The current resulting from the 1800 s potentiostatic hold are
226 shown in Figure 7. We note a roughly linear current response in the log-log
227 representation for short times, in good agreement with other investigations[11,
228 9, 13, 12]. At longer times, there is a pronounced drop-off in the current from
229 the SWNH electrode, possibly indicating that all of the electrochemically active
230 carbon in the electrode has been consumed. Integrating the curves yields the
231 charge passed, which we find to be $10\times$ larger in the case of the SWNH electrode
232 (15.2 C vs. 1.46 C). For a 100% efficient 4-electron oxidation of carbon to carbon
233 dioxide, this is equivalent to approximately 37% of the total carbon in the
234 cathode at the start of the test. Given that 100% coulombic efficiency for CO_2
235 formation is unlikely (due to the formation of surface oxides[9]) we treat this
236 value as an upper bound. **In an identical 1.0 V test of a state-of-the-art carbon-**
237 **free SAFC cathode[6], we also find oxidation currents of approximately 1.5 mA**
238 **$\text{mg}_{\text{Pt}}^{-1}$ at 1.0 V, but no appreciable change in cell performance or resistance**
239 **after 1800 s (see Supplementary Information). This indicates that currents**
240 **attributable to oxidation of Pt and of any current collector materials, in addition**
241 **to carbon oxidation, can be observed via this method and further bounds the**
242 **carbon consumption during the test.**

243 Previous work in liquid acid environments identified a positive correlation
244 between the degree of carbon graphitization and its resistance to corrosion[11,
245 47, 17, 19]. Other guidelines for corrosion resistance were inferred from an
246 extensive statistical analysis and included lower surface area, low roughness,

Figure 7: Chronoamperometric response from experimental cathodes held at 1.0 V in humidified N_2 . Cell temperature was 250 °C with anodes under H_2 and all gases hydrated to 75 °C dew point.

247 and low populations of surface oxides[48]. Amorphous domains and defect sites
 248 were suggested as being especially vulnerable to corrosion[47, 17, 19].

249 Clearly there is some correspondence between these investigations and what
 250 we observe at 250 °C in SAFC cathodes, namely, that MWNT supports are
 251 significantly more stable than SWNHs. We observe enhancement in SWNH D-
 252 band intensity via Raman spectroscopy (Figure 3) which has been previously
 253 been attributed to sp³-bonded[49], that is, non-graphitic carbon in SWNH ag-
 254 gregates. SWNHs also boast enhanced surface area with respect to the MWNT
 255 samples (540 m² g⁻¹ vs. 155 m² g⁻¹). However we must note that in our
 256 solid-state electrodes, the amount of electrochemically active carbon is essen-
 257 tially unknown, in stark contrast with the liquid cell approach used in earlier
 258 work, in which it is assumed that all of the carbon present is active. Given this
 259 categorical difference, the enhanced mixing of CDP with the SWNHs (Figure 4)

260 may also contribute to an enhanced corrosion current.

261 A second key point must be made regarding the differences between CsH_2PO_4 -
262 based cells and PEMFCs or PAFCs. These technologies are particularly affected
263 by carbon corrosion during start-up events, when high voltages can result due to
264 nonuniform fuel distribution in the stack[50]. SAFCs are inherently protected
265 from this effect due to the low proton conductivity of CDP at temperatures
266 below 230 °C.

267 Electron micrographs of sectioned cells recovered after completion of the
268 standard testing protocol suggest loss of carbon under normal (non-accelerated)
269 conditions. Large areas of the post-test SWNH electrode are observed with no
270 carbon visible, which we confirm also via TEM (see Supplementary Informa-
271 tion). In contrast, we note no gross changes to the apparent carbon volume
272 fraction in the case of the MWNT electrode. However we do note in this case an
273 evolution in the CDP morphology towards larger primary particles and, in some
274 areas, an apparent nanoscale mixing with the MWNT supports. This “wick-
275 ing” of the CDP electrolyte into the Pt/MWNT bundles could occur due to
276 formation of the liquid-like intermediate phase of CDP[51, 52] and may explain
277 the pronounced increase in performance over the course of the initial testing
278 cycles, and continuation of this process could impact cell stability over longer
279 timescales.

280 In both experimental electrodes we note significant coarsening in the Pt
281 particle size to a minimum of 10 nm (see Supplementary Information), in a
282 similar range to Pt recovered from state-of-the-art SAFC cathodes containing
283 no carbon[6, 7]. It is likely that here, as in our previous work, that particle
284 coalescence is a primary coarsening channel due to the high metal loadings
285 (60 wt%) and the attendant initial particle clustering that we observed in the
286 pristine samples (Figure 2).

287 An additional experimental cell with a MWNT-based cathode was operated
288 for approximately 140 additional hours after completion of the standard cyclic
289 protocol. The cell was held at a temperature of 250 °C and a constant voltage
290 of 0.6 V with gases hydrated to a 65 °C dew point (see Supplementary Informa-

Figure 8: (a) Uncorrected (b) iR-free and (c) Pt mass-normalized SAFC polarization curves recorded at 250 °C with H₂/air at 75 °C dew point for MWNT-based cathode (1.3 mg_{Pt} cm⁻²) and state-of-the-art 20%Pt@CDP cathode (1.75 mg_{Pt} cm⁻²). Inset in (a) shows an enlargement of the kinetic region.

tion). Over 164 hours, the cell lost approximately 8% of its maximum current (from 243 mA cm⁻² to 223 mA cm⁻²). This current degradation includes the effects of Pt particle coalescence in the cathode and any structural effects related to sintering of CDP domains in either electrode as well as the impact of support corrosion.

Given the stability of the MWNT cathodes, we prepared a state-of-the-art (carbon-free) SAFC cathode following our previously published procedures[6] with cathode Pt loading of 1.75 mg_{Pt} cm⁻². Polarization curves for the baseline cathode and the experimental MWNT cathode are compared in multiple representations in Figure 8. By any metric, the MWNT electrode exhibits enhanced performance with respect to the baseline electrode. We find an enhancement in current density of nearly 100% (52 mA cm⁻¹ vs. 28 mA cm⁻¹) at 0.8 V (Figure 8a, inset) and a striking disparity when activity is normalized to the mass

of Pt in the cathode ($40 \text{ mA mg}_{\text{Pt}}^{-1}$ *vs.* $16 \text{ mA mg}_{\text{Pt}}^{-1}$), as shown in Figure 8c. The experimental MWNT cell also exhibits a 31% increase in maximum power density with respect to the baseline cell (246 mW cm^{-2} *vs.* 187 mW cm^{-2} ; see Supplementary Information). However we do also note again the contrast with the polarization response of the MWNT electrode in the apparent absence of mass-transport limitations in the case of the Pt@CDP baseline electrode, stemming from its macroporous structure.

4. Conclusions

Nanostructured fullerenic carbons comprising single-walled carbon nanohorns and multi-walled carbon nanotubes display vastly different properties as cathode catalyst supports in solid-state intermediate-temperature fuel cells based on the CsH_2PO_4 electrolyte. SWNHs synthesized by pulsed laser vaporization lead to well-dispersed, highly active electrodes with poor voltage stability due to a predisposition to electrochemical carbon corrosion. MWNT-based cathodes require a relatively lengthy activation period during which electrode activity increases considerably, eventually reaching near-parity with the SWNH-based formulation. The greater observed voltage stability of MWNT supports is attributable to a lower defect density and more graphitic character than SWNHs. Either formulation is capable of exceeding state-of-the-art SAFC cathode activity while containing 25% less Pt catalyst. Given their combination of activity and stability in SAFC cathodes, it is likely that MWNTs can be viable catalyst support in intermediate-temperature solid-state electrochemical devices operating at temperatures of at least 250°C .

5. Acknowledgements

This work is supported by ARPA-E under Cooperative Agreement Number DE-AR0000499. SWNH synthesis and Raman spectroscopy were conducted at the Center for Nanophase Materials Sciences, a Department of Energy Office

331 of Science User Facility. We thank Beth Armstrong for assistance with surface
332 area measurements.

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