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Arifin, Nor Anisa; Troskialina, Lina; Shamsuddin, Abd Halim; Steinberger-Wilckens, Robert

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3 **Effects of Sn Doping on the Manufacturing, Performance and**
4 **Carbon Deposition of Ni/ScSZ Cells in Solid Oxide Fuel Cells**

5

6 *Nor Anisa Arifin^{1,2*}, Lina Troskialina^{1,3}, Abd Halim Shamsuddin² and Robert Steinberger-*
7 *Wilckens¹*

8

9 ¹Centre of Fuel Cell and Hydrogen Research, University of Birmingham, B15 2TT, United
10 Kingdom

11 ²Institute of Sustainable Energy, Universiti Tenaga Nasional, 43000 Kajang, Selangor,
12 Malaysia

13 ³Chemical Engineering Department, Politeknik Negeri Bandung, Bandung, 40012 Jawa Barat,
14 Indonesia

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24 [*] Corresponding author: anisa.arifin@uniten.edu.my

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Abstract

This work demonstrates the effect of tin (Sn) doping on the manufacturing, electrochemical performance, and carbon deposition in dry biogas-fuelled solid oxide fuel cells (SOFCs). Sn doping via blending in technique alters the rheology of tape casting slurry and increases the Ni/ScSZ anode porosity. In contrast to the undoped Ni/ScSZ cells, where open-circuit voltage (OCV) drops in biogas, Sn–Ni/ScSZ SOFC OCV increases by 3%. The maximum power densities in biogas are 0.116, 0.211, 0.263, and 0.314 W/cm² for undoped Ni/ScSZ, undoped Ni/ScSZ with 3wt% pore former, Sn–Ni/ScSZ and Sn–NiScSZ with 1wt% pore former, respectively. Sn–Ni/ScSZ reduces the effect of the drop in the maximum power densities by 26% to 36% with the fuel switch. A 1.28 to 2.24-fold higher amount of carbon is detected on the Sn–Ni/ScSZ samples despite the better electrochemical performance, which may reflect an enhanced methane decomposition reaction.

52 **1 Introduction**

53 Solid oxide fuel cells (SOFC) are efficient high-temperature fuel cells with ceramic electrolyte
54 that operate between 600°C and 1000°C[1]. Coupled with combined heat and power system
55 (CHP), the SOFC efficiency can reach up to 90%[2,3]. The key distinction between SOFCs
56 and low-temperature fuel cells is that aside from pure hydrogen the former can operate with
57 alternative fuels, including bio-hythane[4,5], ethanol[6–8], kerosene[9], propane [10–12],
58 ammonia[13,14], syngas[15], methane[16–20], and biogas[14,21–26], where CO also serves
59 as a reactant in the electrochemical reactions[14,19,27–29]. This ability is a remarkable
60 advantage given the high cost of pure hydrogen required in low-temperature fuel cells although
61 when hydrogen produced from renewable energy [30,31]. Furthermore, methane (natural gas)
62 distribution infrastructure already exists whereas the hydrogen distribution network will need
63 to be built from scratch.

64
65 Biogas from wastewater treatment plant contains 60 to 80% CH₄, 30 to 50% CO₂, and traces
66 of impurities [32,33]. Biogas utilisation as an alternative fuel is significant, as based on 2012
67 data, the global biogas production exceeded 56 billion m³/year with the energy potential of
68 1212 PJ [34] led by European countries. Pairing this abundant and under-utilized fuel with
69 SOFC with higher efficiency would increase the generated electricity while considerably
70 reducing the carbon footprint of energy services. In addition, studies by Johnson et al.[35] and
71 Hagen et al.[36] show that the presence of CO₂ (instead of pure methane) in biogas can suppress
72 the effect of sulphur poisoning.

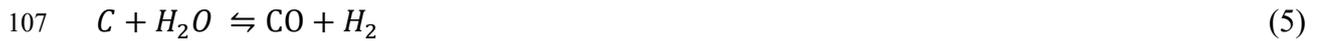
73
74 The conventional strategy for using hydrocarbon fuels is by implementing a separate (external)
75 reforming chamber [37], which induces additional capital and operating costs, and additional
76 effort for supplying the heat to the reforming reactor. The SOFC module is then fed with

77 hydrogen or syn-gas from the reforming chamber to avoid the deteriorating effect of carbon
78 deposition on the SOFC anode[37,38]. On the hand, integrating the reforming reaction into the
79 fuel cell itself (internal reforming) allows for internal heat recycling and thus higher efficiency,
80 but also increases the danger of carbon deposition due to the varying conditions and chemical
81 composition of the fuel gas along the flow path through the fuel cell.

82

83 For a SOFC fuelled by hydrogen, only the electrochemical conversion to electricity and heat,
84 with the reaction product water occurs (Eq.1)[14]. For carbon fuelled-SOFC with internal
85 reforming, more chemical and electrochemical reactions may occur due to the existence of six
86 species (CH_4 , H_2 , CO_2 , CO , H_2 , and C) in the anode side from the feed and the product of
87 different reactions[19,22]. The steam and dry reforming reactions occur internally (Eq. 2a and
88 b, respectively) with hydrogen (H_2) and carbon monoxide (CO) as the products [14,19,22].
89 Steam reforming reaction (Eq. 2a) may take place even without steam addition on the anode
90 surface from the product of H_2 electrochemical reaction (Eq.1) [14,19]. The dry reforming
91 reaction (Eq. 2b) is an overall reaction of two other major reactions: high temperature methane
92 decomposition (Eq. 3) and carbon oxidation by CO_2 (Eq. 4) [19,22]. Methane decomposition
93 (Eq.3) can occur on both anode substrate (AS) and at the anode functional layer (AFL) [19].
94 From inspection of Eq.3 and Eq.4, it is clear that both part-reactions need to be in balance since
95 a lack of carbon oxidation according to Eq.4 would otherwise lead to excess carbon remaining
96 on the catalyst surface, essentially forming a soot cover that will deactivate the catalyst on
97 anode[39]. At SOFC operating temperature, water–gas shift reaction (Eq. 6) (or the reverse
98 reaction) may also accompany the reforming reaction [14,22]. The electrochemical reaction
99 (Eqs. 1 and 7) tend to occur at the anode functional layer (AFL) region, where more triple-
100 phase boundary (TPB) areas are found.

101



110

111 Deposited carbon can be removed with carbon oxidation with CO_2 (Eq. 4) or steam (Eq.5),
112 which will occur via a sufficient supply of the oxygen sources from steam reforming (Eq. 2a),
113 dry reforming (Eq. 2b). Sumi et al.[40,41] and Farrell et al.[8] shows that significantly less
114 carbon in the area within closer proximity to the electrolyte layer, i.e higher carbon oxidation
115 reaction occurred in the TPB area than that on the further position. Hence, it shows that the
116 oxygen ions that diffuse through the electrolyte in fuel cell operation can also be utilised.
117 SOFC are therefore more prone to carbon formation when idling at open circuit voltage (OCV).

118

119 With conventional SOFC cells, the Ni/YSZ anode performance drastically drops when the
120 system is switched from hydrogen to pure methane or biogas fuels expected due to carbon
121 deposition[24,27,42,43]. Carbon deposition may block the TPB and pores on the anode, leads
122 to total anode deactivation, and further halt the SOFC operation[18]. As carbon oxidation also
123 depends on the catalytic activity of the anode material, extensive work focuses on improving
124 the anode catalytic activity for carbon oxidation.

125

126 Although Ni is an excellent catalyst for both electrochemical oxidation reaction and reforming
127 reaction in producing hydrogen and syngas (H_2 and CO)[44–48], Ni also prone to carbon
128 deposition. Hence, Ni-free anode with alternative metal[6,17,49] and perovskites material
129 [50,51] that show better tolerance towards carbon are widely investigated. Still, Ni is widely
130 preferred as the metal catalyst in SOFC anode due to poor catalytic activity in the
131 electrochemical reaction, incompatibility with thermal expansion of other SOFC layers, and
132 low mechanical strength of the alternative materials when compared to Ni[22].

133

134 Another strategy, avoiding the replacement of Ni, is by reducing the affinity of Ni to carbon
135 by replacing the support oxides (YSZ) or by alloying with other metals[39]. Replacing yttria-
136 stabilized zirconia (YSZ) with scandia-stabilized zirconia (ScSZ) or gadolinia-doped ceria
137 (GDC) can successfully improve the tolerance of the anode when tested in methane and biogas
138 [40,52,53] due to higher availability of oxygen ions for carbon oxidation. ScSZ with higher
139 conductivity than YSZ displays different types of carbon[40,43] and carbon deposition
140 behaviour[40,54,55] compared with Ni/YSZ cells, which is due to the difference in crystalline
141 structure [40,43].

142

143 Surface alloying with precious metal such as Pt, Pd, Au, Ru, and Rh[56,57], or base metals,
144 such as Sn, Sm, Co, Fe, Cu, and Ag[24,58,59] can modify Ni in such a way that it preferentially
145 oxidizes C atoms to CO and CO_2 rather than forming C–C bonds[58]. Jiang et al.[24] showed
146 that alloying Ni with Sn achieves the best performance compared with Ag and Cu. Across
147 several works, the electrochemical performance of Sn–Ni/YSZ cells is unchanged or within
148 5% of drop when the fuel is switched from hydrogen to methane or dry biogas, whereas that of
149 Ni/YSZ cells substantially drops[18,27,60].

150

151 Using density functional theory and temperature-programmed reduction with humidified
152 hydrocarbon fuels on Sn–Ni/YSZ, Nikolla et al. [58] suggested that (i) Sn/Ni catalyst has
153 higher efficiency in forming C-O bonds than C-C bonds compared to Ni, which resulted in less
154 solid carbon deposited on the anode, (ii) Higher active sites of Sn/Ni compared to under-
155 coordinated Ni active sites, and (iii) Sn/Ni lessen the binding strength of carbon atoms on the
156 anode. In agreement with studies by Nikolla et al.[58], Kan et al.[18] and Farrel et al.[8] shows
157 less amount of carbon detected on most of the Sn doped cells with humidified fuel or high
158 oxygen to carbon ratio fuel. Kan et al.[18] shows improved stability with operation up to 137
159 hours with Sn-Ni/YSZ cell compared to 27 hours with undoped cells in humidified methane.
160 On the other hand, Singh et al. [42] and Lay et al. [61] reported no significant performance
161 difference and higher amounts of carbon observed on the Sn doped cells compared to the
162 undoped cells with either low steam to carbon ratio. Troskialina et al.[27] and Jiang et al.[60]
163 tested Sn-Ni/YSZ with dry biogas fuel instead of humidified hydrocarbon fuel. All studies
164 [8,27,42] agreed on small amount of Sn (1wt%) as the optimum quantity, in which a higher
165 concentration of Sn decreases the performance due to an increase in polarisation resistance.

166

167 To date, the effect of Sn/Ni alloying has only been tested on Ni/YSZ cells mostly via the surface
168 impregnation method. The metal surface impregnation method introduces several additional
169 steps where the catalyst needs to be repeatedly dispersed on the targeted surface followed by
170 drying and calcination to remove the precursor [27,42]. The work reported here attempted to i)
171 investigate the impact of Sn doping on the electrochemical performance of biogas internal
172 reforming on Ni/ScSZ and the amount of carbon deposited, and ii) test alternative and simpler
173 dopant introduction methods by blending in with the tape casting slurry.

174

175

176 **2 Experimental**

177 **2.1 Materials**

178 The as-received commercial powders used for electrolytes were 10ScCeSZ ((Sc₂O₃)_{0.1}–
179 (CeO₂)_{0.01}–(ZrO₂)_{0.89}); from DKKK with an average particle size of $0.514 \pm 0.053 \mu\text{m}$ (d₅₀).
180 For the anode substrate (AS), coarse nickel oxide (NiO) with a particle size of 8.101 ± 0.185
181 μm (d₅₀) from Novamet and pre-calcined 10ScCeSZ (DKKK) with a particle size of $0.372 \pm$
182 0.001 (d₅₀) were used with a weight ratio of 65:35. Fine as-received NiO (Pi-Kem Ltd.) with
183 an average particle size of $0.637 \pm 0.145 \mu\text{m}$ and as-received 10ScCeSZ (DKKK) were mixed
184 in the same ratio for the anode functional layer (AFL). SnCl₂·2H₂O (Sigma Aldrich, UK) was
185 used as the precursor of Sn to produce Sn-doped Ni/ScSZ cells. As-received lanthanum
186 strontium manganese, La_{0.80}Sr_{0.20}MnO₃ (LSM, Praxair) with an average particle size of 0.90
187 μm was used for cathode.

188

189 **2.2 Methodology**

190 *2.2.1 Sn–Ni/Scsz Cell Fabrication Via Aqueous Tape Casting*

191 Figure 1 shows the two ball-milling mixing steps performed for the full-cell fabrication of the
192 standard Ni/ScSZ cells, as reported in previous work [53]. For Sn-doped cells, SnCl₂·H₂O
193 (1wt% of Sn/Ni) was pre-dispersed with NiO powder by ball milling for 1 h at 120 rpm with
194 water and dispersant. Then, 0wt% and 1wt% pore former were used in this Sn–NiScSZ
195 formulation in accordance with the practicality of the manufacturing method and the targeted
196 porosity of the cells. A high amount of plasticizer and binder was used in leverage to the pore
197 former amount for cells with less pore former, and the 1:1 ratio of binder to plasticizer and
198 solid loading of 55 wt% was maintained. The same formulation with 0wt% and 3wt% pore
199 former was used for undoped Ni/ScSZ cells. The porosity of the reduced anode shown in Table
200 2 was measured via the Archimedes method.

201 A reverse or co-casting tape-casting method [53,62,63], with inverted layer application to the
202 conventional method was used with an aqueous-based formulation. A thin layer of electrolyte
203 was cast first, followed by AFL and AS with drying periods in between. Tape casting was
204 carried out with a laboratory scale tape-casting machine (L800 by MTI) on a silicone-coated
205 PET film. Drying was performed in a low-temperature oven with no air blown to avoid cracks.
206 Table 1 shows the settings applied for tape casting. The button cells with 3 cm diameter
207 produced were co-sintered at 1280°C for 4 h with 1°C/min heating rate and an organic burnout
208 stage at 550°C. 10 g of dead-weight was used to ensure the cell flatness. During high
209 temperature sintering, Cl in the SnCl₂.H₂O is removed, leaving the oxides form. This has been
210 shown in XRD and XPS analysis in previous work in the same research group[22,60]. The
211 LSM cathode ink was produced using a three-roll mill machine (BUHLER) for mixing the
212 cathode powders with a Haraeus V-737 ink vehicle (22.6 vol% solids). The sintered half-cells
213 were hand-painted with a 15 μm thick LSM layer with an effective area of 2 cm² and sintered
214 again at 1100°C.

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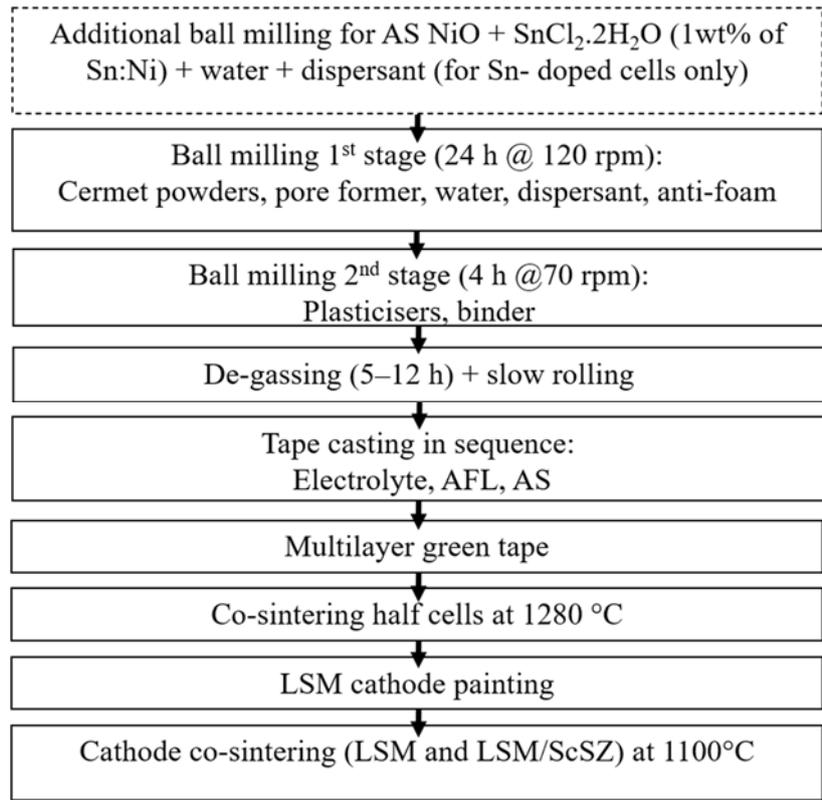


Figure 1. SOFC full-cell manufacturing.

Table 1: Tape-casting setting for different layers.

	Electrolyte	AFL	AS
Speed (mm/s)	3.33	6.33	6.33
Gap (µm)	10-12	15	200
Drying temperature/time	70 °C/10 to 15 min	70 °C/10 to 15 min	33 °C/Overnight

Table 2. Description of fabricated in-house cells.

	Description	Porosity (%)
USC	NiSc	28.5
USC3P	NiSc with 3wt% pore former	39.8
TSC	Sn-NiSc	31.0
TSC1P	Sn-NiSc with 1wt% pore former	38.5

247 *2.2.2 Electrochemical Performance*

248 The testing setup was similar to the one previously described in [53]. Leakage test carried out
249 with He at 750°C prior to feeding with hydrogen. The cells were characterized for 24 h at 750°C
250 in hydrogen by using 21 ml/min H₂ and 7 ml/min He, followed by 24 h in dry biogas at a
251 flowrate of 14 ml/min CH₄, 7 ml/min CO₂ and 7 ml/minute He. The comparison was made
252 using the open-circuit voltage (OCV), maximum power densities, and electrochemical
253 impedance spectroscopy (EIS), measured in turns. EIS analysis was performed at 0.7 V within
254 a frequency range of 0.1 Hz to 1M Hz with a signal amplitude of 10 mV.

255

256 *2.2.3 Post-test Analysis*

257 Microstructural analysis was conducted with a scanning electron microscopy (Hitachi
258 TM3030) with a magnification of 5k and acceleration of 15kV with unpolished and uncoated
259 fragments from tested SOFC cells. Temperature-programmed oxidation (TPO) tests were
260 conducted to quantify the amount of carbon in the SOFC-tested cells. 200gram of SOFC-tested
261 fragments were placed in the middle of a quartz chamber with compressed air flow rate of 50
262 ml/min for carbon oxidation. The furnace was ramped to 600°C at 5°C/min and annealed for 1
263 h to allow complete carbon oxidation. The outlet gas tube was connected to a mass
264 spectroscopy machine (MKS-Cirrus, USA) for evaluation. TPO was calibrated using three
265 known amounts of carbon graphite powder (10.1, 1.2 and 0.7 g) prior to the actual sampling.
266 The resulting CO₂ peak areas were used to construct a calibration curve (supplied in
267 supplementary material section). The calibrated value obtained used as a factor to quantity the
268 amount of carbon on the tested cells.

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272 **3 Results and discussion**

273 **3.1 Effect of Sn Doping on Full-Cell Manufacturing**

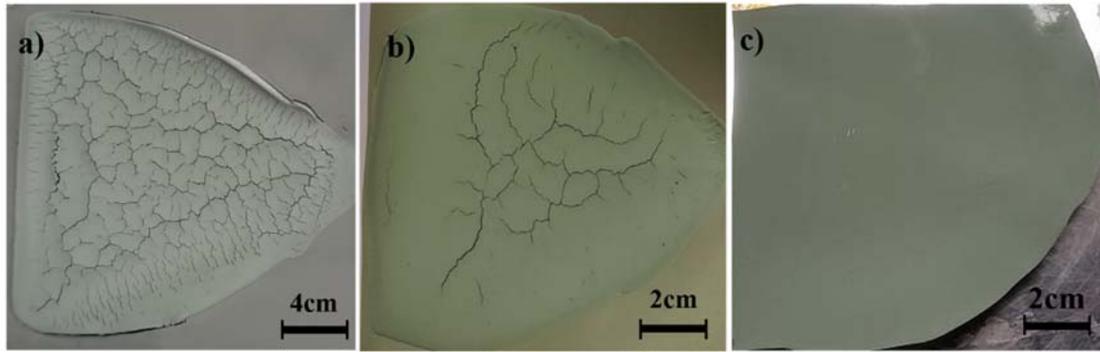
274 The addition of $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ to the anode substrate slurry in either the first or second stage
275 resulted in a thick slurry, which cracked when completely dried (Figure 2). The mud-cracked
276 tape in Figure 2 originated from the uneven drying or drying gradient between the bulk of the
277 slurry and the skin of the tape. Blend-in doping with the tape-casting slurry was achieved by
278 introducing an additional premixing described in the methodology section. Mixing via ball
279 milling with only NiO powder increased the probability of Sn adherence to the Ni surface rather
280 than the ScSZ. The microstructural analysis of the sintered full cell (Figure 3a) revealed the
281 microstructure of TSC (Sn–Ni/ScSZ cells) with dense electrolyte and porous anode substrate.
282 Figure 3c shows the anode substrate of TSC after NiO reduction, which created a more porous
283 structure compared with the anode substrate before reduction (Figure 3b). The average anode
284 porosity of TSC was 31.0%, which was higher than that of undoped cells (USC) (28.5%),
285 although the same setting was used. TSC1P (Sn–Ni/ScSZ with 1wt% pore former) and USC3P
286 (undoped Ni/ScSZ with 3wt% pore former) were fabricated with a final porosity volume of
287 38.5% and 39.8%, respectively. With the 55wt% solid loading used, the addition of more than
288 1wt% pore former in the Sn–Ni/ScSZ formulation resulted in a thick slurry, which limited
289 further addition of pore former. Increased porosity in the anode substrate leads to a decrease in
290 mass diffusion resistance, i.e higher performance, as long as the porosity level still within
291 optimum porosity level (<40%) [64,65]. Hence, due to the influence of Sn addition to porosity,
292 cells with similar porosity levels were targeted and tested.

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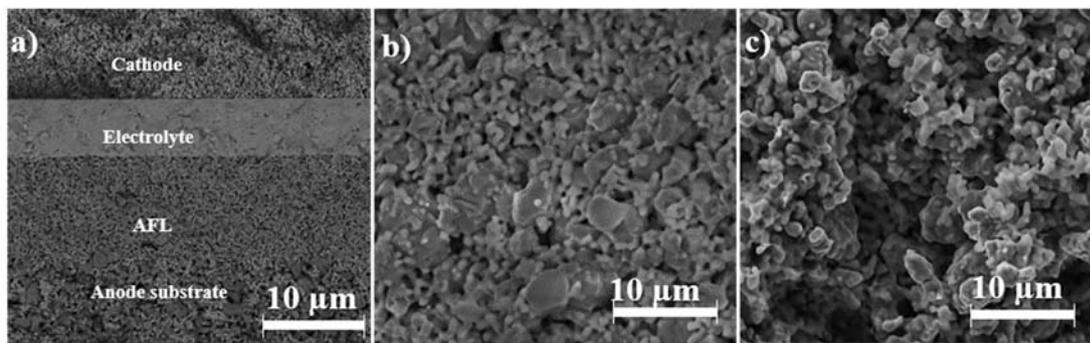


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298 **Figure 2.** Ni/ScSZ green tape with blend-in $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ with different addition stages; a) after
 299 the first ball milling, b) after the second ball milling, and c) additional premixing step with
 300 NiO, dispersant and water.

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305 **Figure 3.** TSC before SOFC cell test, a) cross-section image, b) anode substrate before
 306 reduction, and c) anode substrate after reduction.

307

308 3.2 Electrochemical performance

309 3.2.1 Open circuit voltage

310 Initially in the hydrogen test, the test was run under OCV mode for six hours for complete
 311 reduction of the cells while the first run of SOFC in biogas was 90 minutes in OCV mode to
 312 minimise carbon deposition. The OCV measured alternately with iV curve, impedance, and
 313 potentiostatic. Figure 4a shows that in TSC (Sn-Ni/ScSZ with 0 wt% pore former), the open-
 314 circuit voltage (OCV) in hydrogen was stabilized at 1.03 V 80 minutes after hydrogen was
 315 introduced and gradually dropped to 1.02 V. With the fuel swap from hydrogen to biogas (BG),
 316 the OCV value was higher than that generated in hydrogen (1.05 V). Figure 4b shows the same
 317 trend observed in TSC1P (Sn-Ni/ScSZ with 1 wt% pore former), whilst the opposite trend was

318 observed with the undoped Ni/ScSZ cells (USC and USC3P). OCV also increased in Sn–
 319 Ni/YSZ cells reported previously by Troskialina et al. [27].

320 The Nernst equation for the electrochemical reaction for H₂ (Eq.1) is presented by Eq.8, which
 321 in analogy also applies to Eq.7, the CO oxidation. E⁰ is the open-circuit voltage (OCV), also
 322 called the reversible potential or electromotive force (EMF), can be calculated from the Gibbs
 323 free energy for the respective reaction and the Faraday constant as shown in Eq.9. Gibbs free
 324 energy of CO oxidation at 750°C is higher than that of H₂ oxidation, which are –191.5 kJ/mol
 325 and -193.6 kJ/mol [66], respectively. Substituting these values in Eq.9, the theoretical OCVs
 326 at 750°C are 1.03V and 0.99V for H₂ and CO respectively. Higher OCV value from the CO
 327 electrochemical oxidation expected to increase the OCV when biogas is used, but the OCV
 328 dropped instead in the undoped cells. The difference in OCV value in biogas setup between the
 329 Sn doped and undoped cells may reflect the difference in dry methane reforming (Eq.2b)
 330 ability, which has higher OCV value as reported by You et al. [19].

331

$$332 \quad E = E^0 + \frac{RT}{2F} \ln \left(\frac{p_{H_2} p_{O_2}^{1/2}}{p_{H_2O}} \right) \quad (8)$$

$$333 \quad E^0 = -\Delta G_{rxn}^0 / 2F \quad (9)$$

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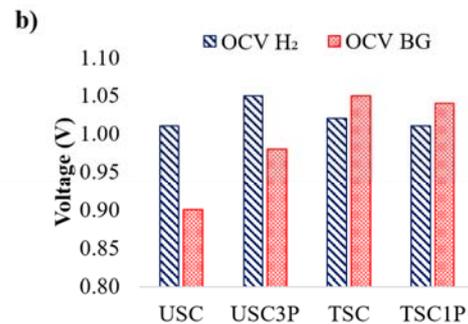
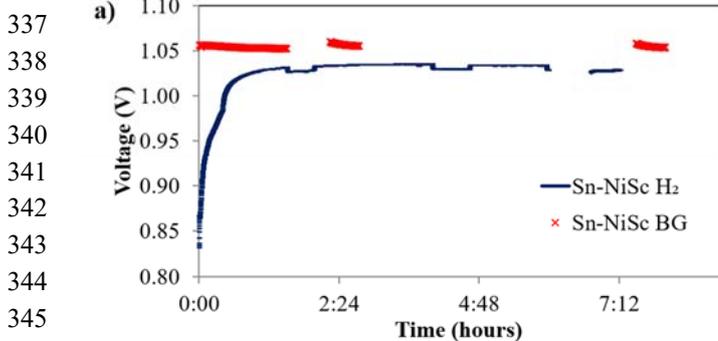


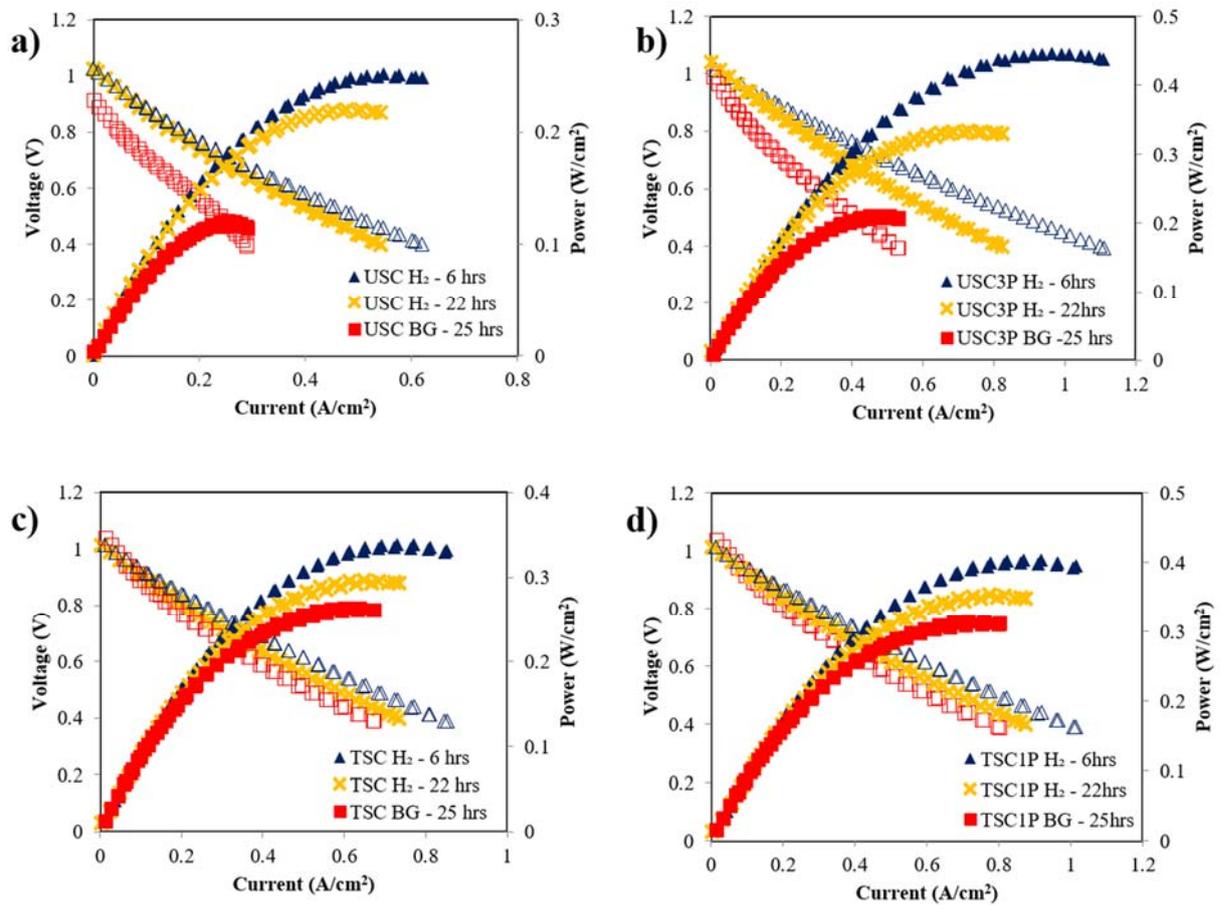
Figure 4. OCV when tested in hydrogen (H₂) and biogas (BG) of a) Sn–Ni/ScSZ SOFC cell (TSC) and b) across different cells, Sn-doped and undoped cells.

350 3.2.2 *Maximum power densities and impedance analysis*

351 Figure 5 shows that the first maximum power densities obtained in hydrogen were 0.252, 0.450,
352 0.339, and 0.404 W/cm² for USC, USC3P, TSC, and TSC1P, respectively. In all cells, the
353 constant degradation observed in the *iV*–PV curve may be due to Ni coarsening in the cermet,
354 which reduces the catalytic surface area in the fuel cell. This well-known initial process in
355 SOFC has also been reported by Farrell et al.[8]. With an average 16% of cell degradation, the
356 maximum power densities in hydrogen before the fuel swap were 0.220, 0.331, 0.297, and
357 0.349 W/cm² for USC, USC3P, TSC, and TSC1P, respectively. USC3P observed to have higher
358 degradation in hydrogen (Figure 5) compared to other cells. It is suspected to be due to the
359 high porosity level, which near the maximum recommended limit (40%). Continuous Ni
360 coarsening and agglomeration may push the porosity limit, reduce the TPB volume, hence the
361 catalytic area and affected the effective conductivity[64,65]. The effect of porosity (Table 2)
362 on cell performance (Figure 5) was considerable, and less porous cells experienced high
363 resistance for the fuel to diffuse through the anode substrate (Figure 6). Hence, the slightly
364 lower performance of TSC1P in hydrogen compared with that of USC3P may be due to the
365 porosity level. The maximum power density of the latter was higher than that of the former.
366 Given the influence of Sn dopant to the cell's porosity, surface impregnation on sintered half
367 cells may be a more suitable method due to this limitation.

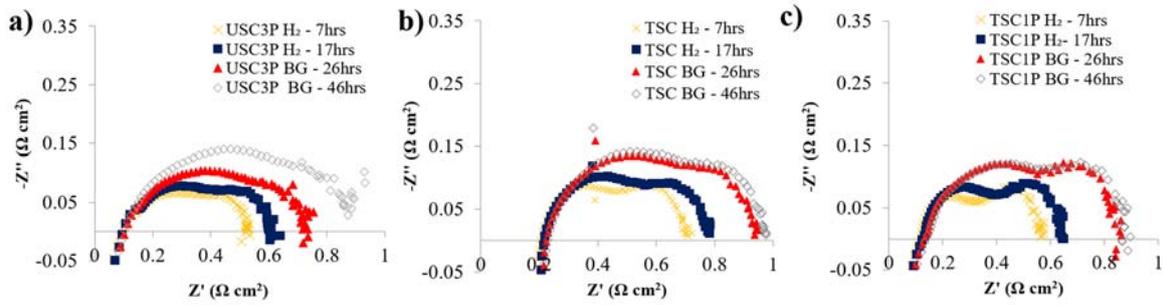
368 When the SOFCs were operated with biogas after the 24 hours test in hydrogen, the
369 performance of the cells dropped. Sn-doped cells were less affected and showed an average of
370 11% drop in performance with the fuel swap, whilst undoped Ni/ScSZ cells exhibited 36% and
371 47% drop in performance for USC and USC3P, respectively. The maximum power densities
372 in biogas were 0.116, 0.221, 0.263, and 0.314 W/cm² for USC, USC3P, TSC, and TSC1P,
373 respectively. In the undoped cells, polarization increased with time in both hydrogen (0.032
374 Ωcm²) and biogas (0.14 Ωcm²). Surprisingly, the increase in biogas polarization in both TSC

375 and TSC1P between 26 h and 46 h was not substantial ($0.030\text{--}0.035\ \Omega\text{cm}^2$), as shown by the
 376 Nyquist plot in Figure 6. No impedance data were obtained for USC due to a spectrometer
 377 failure. Kan et al. [18] observed long-term stability with methane with Sn-doped Ni/YSZ cells,
 378 but the power density values obtained in methane operation between the undoped Ni/YSZ cells
 379 and doped Sn-Ni/YSZ cell were similar. Troskialina et al. [27] observed similar maximum
 380 power density under hydrogen and biogas via surface impregnation with pipette doping; the
 381 performance did not drop, which was also observed by Farrell et al. [8].
 382



383
 384 **Figure 5.** *iV*–*PV* curve of the cells: a) USC, b) USC3P, c) TSC and d) TSC1P in hydrogen
 385 (H₂) and biogas (BG).

386
 387



388

389 **Figure 6.** Nyquist plot of a) USC3P, b) TSC, and c) TSC1P and in H₂ and biogas (BG).

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391

392 3.3 Carbon deposition post-test analysis

393 3.3.1 SEM microstructure analysis

394 The microstructures of the anode of the undoped sample and Sn-doped cells are shown in

395 Figure 7. In both cases, the filamentous growth structures (circled in red) were visually

396 observed by SEM. Baker et al. [67] explained that filamentous carbon may have a graphitic

397 skin and an amorphous head end. A small amount of graphitic carbon enhances the

398 performance by increasing the Ni anode conductivity via the additional graphitic carbon

399 network [68,69]. Carbon quantification with SEM–energy dispersive X-ray analysis (EDX) is

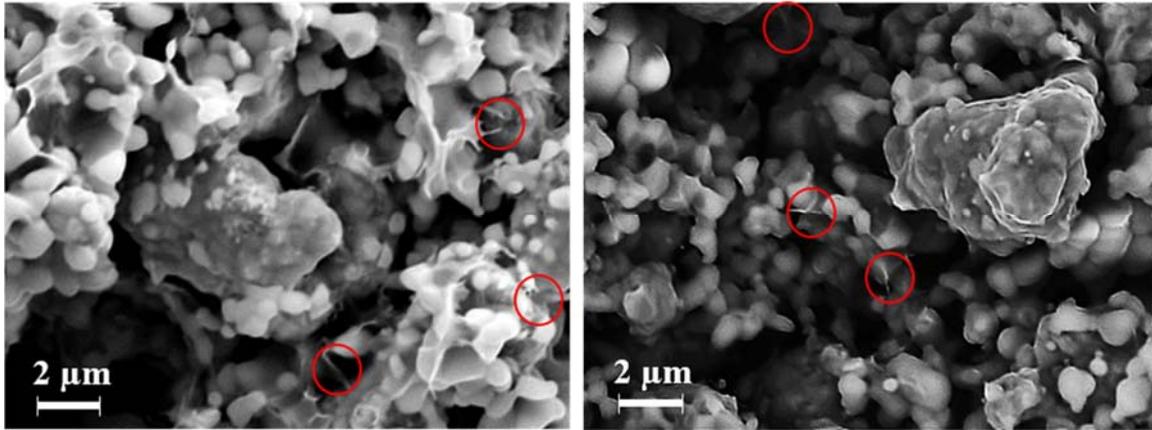
400 unreliable in this case because the electron signal is affected by the anode’s uneven porous

401 structure. Hence, carbon quantification via temperature-programmed oxidation (TPO) was

402 used for evaluating the amount of carbon deposited, corresponding to the amount of CO₂

403 released.

404



405

406 **Figure 7.** Microstructure of a) USC3P and b) TSC after SOFC cell testing with carbon

407 growth circled in red

408

409

410 3.3.2 Carbon quantification via temperature-programmed oxidation

411 The graphitic carbon burn-off in this work started at 520°C and completed the combustion at

412 600°C during the 1-hour dwelling stage (shown in the supplementary material). The CO₂ peaks

413 from the samples observed at 600°C (Figure 8) confirmed that the type of carbon build-up in

414 the samples were graphitic. In USC3P, smaller peaks at 400°C that might originate from

415 amorphous carbon was detected. The amounts of carbon deposited on TSC and TSC1P of Sn–

416 NiScSZ samples were 4.83×10^{-3} and 5.94×10^{-3} mg-C/mg_{cat}, respectively, which were higher

417 than those of undoped Ni/ScSZ cells, USC and USC3P (1.49×10^{-3} and 2.60×10^{-3} mg-C/mg_{cat}).

418 The amount of carbon deposited and the rate of carbon deposition in the samples are presented

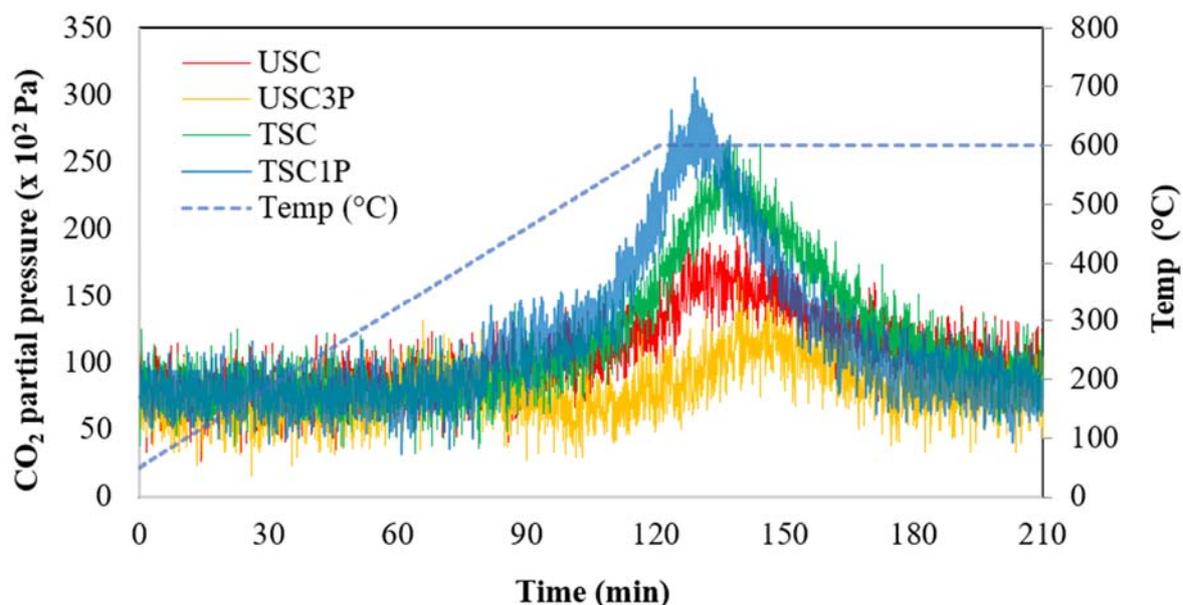
419 in Table 3. The carbon deposited and the rate of carbon deposition calculated in this work was

420 the net balance of carbon deposited, subtracting the amount of carbon oxidized to CO₂ and CO

421 during the SOFC electrochemical reaction. The carbon deposition in Ni/ScSZ (40% Ni) anode

422 investigated by Somalu et al. [70] with a quartz tube and with an S/C ratio of 0.8 without

423 electrochemical reaction was 28 mg-C/mg_{cat}.



424

425

426 **Figure 8.** CO₂ peaks from carbon burn off on Sn–Ni/ScSZ and undoped Ni/ScSZ cells.

427

428

429 **Table 3.** Amount and rate of carbon deposition in undoped and Sn-doped NiScSZ cells.

	Amount of carbon deposited ⁴³⁰		Rate of carbon deposition ⁴³¹ (mg-C/g _{cat} h) ⁴³²
	Per sample (mg)	Per unit catalyst (mg-C/mg _{cat})	
USC	0.300	1.49×10^{-3}	0.062
USC3P	0.525	2.60×10^{-3}	0.108 ⁴³³
TSC	0.975	4.83×10^{-3}	0.201 ⁴³⁴
TSC1P	1.275	5.94×10^{-3}	0.248

435

436 In the present work, although only one burn off temperature that deduced to be graphitic carbon

437 from the burn off temperature (Figure 8), amorphous carbon may also have formed. As

438 amorphous carbon is easier to oxidise, it may have oxidised either from CO₂ (Eq.4), or H₂O

439 (Eq.5), or by oxidation from the electrochemical reaction (Eqs 1 and 6), hence only small

440 amount of amorphous carbon detected in the USC3P in the TPO analysis.

441

442 Initially, the improved performance of Sn–NiScSZ suggested that the amount of carbon
443 deposited may be lower than that on the undoped cells due to the assumption that carbon
444 deposition may have hindered the electrochemical reaction. However, the result from TPO
445 showed otherwise. Thus, the decreased performance of undoped Ni/ScSZ cells in the present
446 study was not mainly due to the amount of carbon deposited but inclined to lack of methane
447 decomposition reaction (Eq. 3), hence lowered the amount of H₂. On the other hand, Sn
448 accelerated the activity of the methane decomposition reaction (Eq. 3), thereby releasing an
449 increased amount of H₂ as reactant for the electrochemical reaction and inevitably accompanied
450 by increased amounts of carbon. The result of this present study supported by Troskialina [71].
451 Troskialina [71] detected a higher amount of carbon in Sn-doped Ni/YSZ cells than in undoped
452 cells, with the carbon peak coinciding with the graphitic carbon burn-off temperature, as
453 observed in the present work.

454

455 In the present study, the author speculates that in the region with closer proximity to the
456 electrolyte (i.e the TPB/AFL area), rapid oxidation occurred due to increased electrochemical
457 reactions (Eq. 1) in response to increase amount of H₂. However, in case of carbon deposited
458 in further position (mainly in the anode substrate region), carbon might be oxidised only by
459 CO₂ (Eq. 4) or by H₂O (Eq. 5). In this case, the carbon oxidation by CO₂ (Eq. 4) and by H₂O
460 (Eq. 5) reaction rates might be slower than that of methane decomposition (Eq.3), leading to
461 increased carbon amount in Sn doped cells. Therefore, although small amount of graphitic
462 carbon may still deposit near the TPB electrochemical reaction region, it did not hinder the
463 reaction. On the other hand, it may enhance the electrochemical reaction and electrical
464 conductivity by the extra graphitic network[68,69]. Nonetheless, even with assumption that the
465 TPB area is unaffected, excessive carbon build up in the substrate region must be avoided as it
466 will lead to stress, fracture the support, or push the metal particles off the support[39].

467

468 The improve electrochemical performance of Sn doped cells in biogas compared with undoped
469 cells agreed with previous findings[18,27,42]. However, the high amount of carbon formed on
470 the Sn-doped cells in the present study was in contrast to the findings of Farrell et al.[8] and
471 the suggestion of Nikolla et al.[58] on the carbon oxidation ability. The significant difference
472 with this study compared to Nikolla et al.[58] and Farrell et al.[8] is the carbon ratios in the
473 hydrocarbon fuel. In present study, dry biogas is used, while Nikolla et al.[58] conducted the
474 studies with moderate steam to carbon ratio with different fuels and Farrell et al.[8] used
475 ethanol, which has higher oxygen to carbon ratio. On other studies, Singh et al.[42] and Lay et
476 al.[61] reported no significant performance difference and higher amounts of carbon observed
477 on the Sn doped cells compared to the undoped cells with either low steam to carbon ratio or
478 dry methane.

479

480 The surface impregnation method showed similar performance in hydrogen and biogas by the
481 Sn-NiYSZ anode when the fuel was switched from hydrogen to humidified methane and biogas
482 [42,71]. Through surface impregnation, almost all dopants adhere to the Ni on the anode
483 substrate surface, which may have better exposure in catalysing the dry reforming reaction as
484 well as increased the electrochemical reaction. On the other hand, doping by the slurry blend-
485 in method practiced in present work may cause the Sn dopant to sit in the cermet bulk and thus
486 not be accessible. Hence, although dopant introduction can be performed easily with slurry
487 blend in method, surface impregnation is more effective. Alternately, relative more dopant
488 would be required, and optimisation need to be carried out to statistically secure sufficient
489 presence on the nickel particle surfaces. Nonetheless, if the main aim of the research is on the
490 influence of Sn as dopant, surface impregnation method is recommended to eliminate the

491 influence of porosity to mass diffusion resistance and conductivity on the electrochemical
492 performance.

493

494 **4 Conclusion**

495 The electrochemical performance result suggested that Sn doping enhanced the performance
496 of Ni/ScSZ cells in biogas operation, due to improved catalytic activity of the methane
497 decomposition reaction, which is the first step in dry methane reforming reaction. The higher
498 amount of carbon deposited originated from slower carbon oxidation compared to the methane
499 decomposition reaction on Sn-Ni/ScSZ. From the higher amount of carbon affected by the
500 methane decomposition reaction, we found no conclusive evidence on the positive influence
501 of Sn on carbon oxidation on Ni/ScSZ. In further work, a more in-depth understanding on the
502 effect of Sn addition in the dry reforming and carbon oxidation reactions may be possible
503 through prolonged SOFC electrochemical tests and separate reforming catalytic activity tests
504 with Sn–Ni/ScSZ cell with the exhaust gas connected to a gas chromatograph–mass
505 spectrometer. Separate conductivity tests in further work will also assist the understanding of
506 the effect of Sn to anode’s porosity and conductivity.

507

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514

515

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