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> Are metal-free pristine carbon nanotubes electrocatalytically active? Yi Cheng, Jin Zhang, San Ping Jiang Fuels and Energy Technology Institute, Curtin University, Perth, WA 6102, Australia <u>S.Jiang@curtin.edu.au</u> (SP Jiang)

## **Supporting materials**

## Experimental

CNTs with different number of walls and diameters were obtained from commercial sources including Nanostructured & Amorphous Materials, Inc., USA, Beijing Dk Nano Technology Co. Ltd and Shenzhen Nano, China. The as-received CNTs were purified as reported elsewhere.<sup>1</sup> Due to the relatively mild purification procedure, the amount of metal impurities was in the range of 0.4-1.3% as determined by the ICP-OES analysis (Table S1). The metal impurities are mainly Fe, Co, Mo and Ni and no Mn was found in the CNTs sample. KOH (Sigma-Aldrich), Nafion solution (Sigma-Aldrich, 5% in isopropanal and water), KCN (Sigma-Aldrich) were received and used without further treatment. CNTs were characterized using a transmission electron microscope (TEM JEOL3000) operating at 200 kV. The average outer diameter (OD) and number of walls of CNTs were estimated by measuring 100 randomly chosen CNTs in the TEM images.<sup>2</sup> The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a XPS apparatus (Kratos AXIS Ultra DLD) with pass energy of 40 eV.

The electrochemical measurements were conducted in a typical three electrode cell with a Luggin capillary. The tip of the Luggin capillary was placed 3 mm beneath the working electrode. A Pt wire and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All potentials in the present study were given versus RHE reference electrode ( $E_{RHE}=E_{SCE}+0.245+0.059$ pH). The linear scan voltammetry curves (LSV) were conducted at 10 mV s<sup>-1</sup> in 1 M KOH and 1 M KOH + 10 mM KCN solutions. LSV tests for HER and OER were conducted on a rotating disk electrode with a rotation rate of 1600 rpm to avoid the formation of bubbles at the electrode surface at scan rate of 10 mV s<sup>-1</sup>. The ORR on CNTs was measured by the LSV on a rotating disk electrode in O<sub>2</sub>-saturated 1 M KOH at a scan

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rate of 10 mV s<sup>-1</sup> and a rotation rate of 1600 rpm. CNT loading was 0.05 mg cm<sup>-2</sup>. For the experiments in 1M KOH + 10 mM KCN, the electrode was rotated at 1600 rpm for 5 min in order for the CN<sup>-</sup> ions to be fully coordinated with the metal impurities prior to the electrochemical test. Tafel plots were recorded at a sweep rate of 1 mV s<sup>-1</sup> and the Tafel slope is IR corrected. The Ohmic potential drop between the working electrode and the tip of the Luggin capillary was estimated by measuring the impedance value at the frequency of 30 kHz.

## **Results and discussions**

**Fig.S1** shows the TEM micrographs and Raman spectra of CNTs samples used in this study. Based on the number of walls, the CNTs were characterized as belonging to one of seven groups labelled as CNT-n with n = 1-7 (Fig.S2 and S3 and Table S2). CNT-1 mainly composes of SWNTs (79%) with OD = 1.97 nm. CNT-2 is mainly double-walled CNTs (DWNTs, 65%) with OD = 3.30 nm. CNT-3 and CNT-4 are mainly triple-walled CNTs (TWNTs, 52-57%) with OD = 3.80 and 4.00 nm, respectively. The average number of walls of CNT-5 is seven with OD = 5.10 nm. CNT-6 and CNT-7 are typical MWNTs with number of walls over 12 and 30 and OD = 13.90 and 20-40 nm, respectively. For CNT-1, the large radial breathing mode (RBM) observed around 200-300 cm<sup>-1</sup> is typical characteristics for SWNTs (Fig.S1H).<sup>3,4</sup> The ratio of the intensity of the *D* band near 1300 cm<sup>-1</sup> to the *G* band (~1590 cm<sup>-1</sup>),  $I_D/I_G$  is 0.155, 0.51, 0.76, 0.94, 1.35, 2.50 and 2.86 for CNT-1; CNT-2, CNT-3, CNT-4, CNT-5, CNT-6 and CNT-7, respectively. The  $I_D/I_G$  ratio increases with the increasing number of walls and OD as multiple graphite layers lead to a greater quantity of structural defects.<sup>3</sup>

The average outer diameter (OD) and number of walls of CNTs were estimated by measuring 100 randomly chosen CNTs on different TEM images taken in different parts of the CNT samples (Fig.S2 and S3). The results are given in Table S2.

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CNTs		CNT-	CNT-	CNT-	CNT-	CNT-	CNT-	CNT-
		1	2	3	4	5	6	7
As received W/W %	Ash	1.56	4.82	5.1	5.2	5.16	2.16	2.39
	Co	0.08	2.32	2.02	-	0.5	-	-
	Fe	0.43	0.30	0.26	0.29	0.35	0.28	0.54
	Mo	0.04	0.75	0.73	0.79	0.11	-	0.84
	Ni	0.08	0.08	0.04	0.17	0.019	0.25	0.21
Purified W/W %	Ash	1.21	2.08	2.15	2.54	2.28	2.08	1.83
	Co	0.07	0.81	0.57	-	0.38	-	-
	Fe	0.29	0.23	0.23	0.28	0.17	0.21	0.29
	Mo	0.03	0.30	0.27	0.34	0.09	0.01	0.49
	Ni	0.05	0.04	0.03	0.15	0.015	0.2	0.17

Table S1. Metal impurities in as-received CNTs and purified CNTs by ICP.

**Table S2**. BET, outer diameter, number of walls,  $I_D/I_G$  ratios of CNTs samples.

CNTs	CNT-1	CNT-2	CNT-3	CNT-4	CNT-5	CNT-6	CNT-7
Number of walls	1 (79%) 2 (16%) 3 (5%)	2 (65%) 3 (23%) 4 (5%)	2 (25%) 3 (52%) 4 (10%) 5 (8%)	3 (57%) 4 (20%) 5 (19%)	3 (5%) 4 (11%) 5 (25%) 6 (17%) 7 (16%) 8 (17%) 9 (9%)	>12	>30
x	1	2	3	3	7	~12	~30
Outer diameters (nm)	1.97±0.4	3.3±0.89	3.8±0.63	4.0±0.66	5.1±0.98	13.9±5.2	35.2±8.5
Surface area (m <sup>2</sup> /g)	651	679	643	459	485	174	85
$I_D/I_G$	0.16	0.51	0.76	0.94	1.35	2.50	2.86
Defects (XPS)	6.16	4.17	8.16	8.33	7.91	4.77	6.79

\* <sup>\*</sup> is the average of number of walls of CNTs samples, taking as an integer number.



**Fig. S1.** TEM micrographs of CNTs studied. A) CNT-1 with 79% SWCNTs, B) CNT-2 with 65% DWCNTs, C) CNT-3 with 52% TWCNTs; D) CNT-4, mainly 57% TWCNTs, E) CNT-5 with 3-10 walls, F) CNT-6, MWNTs with 12 walls, G) CNT-7, MWNTs with the number of walls exceeding 30, H) Raman spectra of CNT-n with n = 1-7.



Figure S2. Distribution of number of walls of CNT-1 to CNT-5.



Figure S3. A) Distribution of outer diameters of CNTs samples, B) the relationship of number of walls, Raman intensity  $(I_D/I_G)$  and outer diameters.

**Fig.S4** shows the XPS core-level spectra of C1s for different CNTs, Herein, curve fitting of the C1s spectra was performed using a Gaussian-Lorentzian peak shape after performing a Shirley background correction. The main peak observed at 284.5 eV is contributed to the C-C bond of  $sp^2$  carbon in the basal plane of carbon nanotubes. Small peaks, which are assigned to C-O bonds (286.2 eV), the carbonyls (C=O) bonds (287.2 eV) and carboxylates (O-C=O) bonds (288.0 eV), are also found in CNTs, indicating the small amount defects in CNTs. The total amount of C-O, C=O and O-C=O defects is 6.2%, 4.17%, 8.2%, 8.3%, 7.9%, 4.77% and 6.8% for



Fig. S4. XPS core-level spectra of C 1s of different CNTs.

We validated the KCN method by artificially depositing 3.5% of NiCo double oxide onto the CNT-7 (3.5% NiCo/CNT-7), and testing the activity of NiCo/CNT-7 in the absence and presence of 10 mM KCN. As shown in Fig.S5, 3.5% CoNi/CNT-7 exhibits a current density of 27 mA cm<sup>-2</sup> at 1.8 V in 1 M KOH in the absence of KCN, however, in the presence of 10 mM KCN, the current density at 1.8 V is reduced significantly to ~3 mA cm<sup>-2</sup>, which is similar with that of pristine CNT-7. This again confirms that 10 mM KCN in 1 M KOH solution can completely block the activity of NiCo metal catalysts. It is noticed that in this case the loading of NiCo is 3.5wt%, substantially higher than the impurities contents of the CNTs samples used (see Table S1).



**Fig.S5**. LSV curves of OER in 1M KOH with and without 10 mM KCN. Scan rate=10 mV s<sup>-1</sup>, rotating rate=1600 rpm and CNTs loading=0.05 mg cm<sup>-2</sup>.

We re-calculated the activity based on the specific surface area (Table S2) and the results are shown in **Fig.S6**. As shown in the figure, the activity for OER, HER is characterized by a distinctive volcano-type curves as a function of number of walls, exactly the same as that based on the geometrical area-based current density. As shown in Table S2, the specific surface areas of CNT-4 is 485 m<sup>2</sup>/g, significantly lower than 651 m<sup>2</sup>/g of CNT-1, however, the activity of CNT-4 is substantially higher than CNT-1. Based on the results, we can conclude that the volcano-curves of the electrocatalytic activity of CNTs are not related to the specific surface area of the CNTs under the presence conditions of study.



**Fig.S6**. Plots of the activity based on the specific surface area of the CNTs of OER (left) and HER (right) measured in 1 M KOH in the presence of 10 mM KCN.

In alkaline conditions, the OER, ORR and HER can be written as follows: 5-7

- OER:  $4OH^{-} \rightarrow O_2 + 2H_2O + 4e$  (1)
- ORR:  $O_2 + H_2O + 2e \rightarrow HO^{2-} + OH^{-}$  (2)

HER:  $H_2O + 2e \rightarrow H_2 + 2OH^-$  (3)

**Fig. S7** shows the Tafel regions of HER on CNTs electrode. In the Tafel slopes are 400, 210, 210, 260, 320, 350 and 350 mV dec<sup>-1</sup> for CNT-1 to CNT-7 respectively. The Tafel slopes are significantly higher than that reported on polycrystalline Pt<sup>8</sup> and polycrystalline Ni<sup>9</sup> reported in alkaline solutions. The lower Tafel slope of CNT-2 CNT-3 and CNT-4 is consistent with the higher activity for HER on CNTs compared with other types of CNTs. The extremely high Tafel slope indicates that the HER is kinetically difficult on CNTs.



**Figure S7**. Tafel plots for HER on CNTs. The tests were conducted in 1M KOH solution containing 10 mM KCN with catalyst loading of 0.05 mg cm<sup>-2</sup> and stirring rate of 1600 rpm.

**Fig. S8** is the Tafel slopes of CNTs for ORR. CNT-3 and CNT-4 has a slightly lower Tafel slope of 51 mV dec<sup>-1</sup> as compared to 60 mV dec<sup>-1</sup> obtained on CNT-1, CNT-6 and CNT-7. These Tafel slopes are similar with that reported on glass carbon and graphite<sup>10</sup>. These results demonstrated that ORR on CNTs is most likely a 2 electron transfer oxygen reduction process. However, more detailed experiments are planned to study the mechanism of the reaction on different CNTs.



**Figure S8.** Tafel slope for ORR on CNTs in  $O_2$ -saturated 1 M KOH solution containing 10 mM KCN with a scan rate of 1 mV s<sup>-1</sup>. The tests were conducted in 1M KOH solution with catalyst loading of 0.05 mg cm<sup>-2</sup> and stirring rate of 1600 rpm.



**Figure S9**. Tafel plots for OER on CNTs. The tests were conducted in 1M KOH solution containing 10 mM KCN with catalyst loading of 0.05 mg cm<sup>-2</sup> and stirring rate of 1600 rpm.

The higher activity of OER on CNT-2, CNT-3 and CNT-4 is supported by the lower Tafel slope. **Fig. S9** shows the Tafel plots for the OER on CNTs electrode measured in 1M KOH containing 10 mM KCN with catalysts loading of 0.05 mg cm<sup>-2</sup>. For OER, CNT-2, CNT-3 and CNT-4 exhibit a Tafel slope of 125, 90 and 105 mV dec<sup>-1</sup> respectively, this is close to ~120 mV dec<sup>-1</sup>. On the other hand, for the OER on CNT-1, CNT-5, CNT-6 and CNT-7, the observed Tafel slope is ~210 mV dec<sup>-1</sup>, closing to 240 mV dec<sup>-1</sup>, and substantially higher than that for the reaction on CNT-2, CNT-3 and CNT-4. The Tafel slope of ~120 mV dec<sup>-1</sup> observed for the OER on CNT-3 and CNT-4.

2, CNT-3 and CNT-4 is consistent with the fact that the rates determine steps (RDS) for OER is limited by the first electron transfer step<sup>11-14</sup>

 $CNT + OH^{-} \rightarrow CNT - OH + e$  (4)

The high Tafel slope, ~240 mV dec<sup>-1</sup> observed for the reaction on CNT-1, CNT-5, CNT-6 and CNT-7 implies that the energy barrier for the electron transfer associated with the discharge of OH<sup>-1</sup> species on the SWCNTs and MWCNTs would be much higher.

## References

- Y. Cheng, C. W. Xu, L. C. Jia, J. D. Gale, L. L. Zhang, C. Liu, P. K. Shen, S. P. Jiang, *Applied Catalysis B-Environmental*, 2015, 163, 96-104.
  Y. Cheng, C. Xu, L. Jia, J. D. Gale, L. Zhang, C. Liu, P. K. Shen, S. P. Jiang, *Applied Catalysis B: Environmental*, 2015, 163, 96-104.
  U. J. Kim, C. A. Furtado, X. M. Liu, G. G. Chen, P. C. Eklund, *Journal of the American Chemical Society*, 2005, 127, 15437-15445.
  R. Saito, M. Hofmann, G. Dresselhaus, A. Jorio, M. S. Dresselhaus, *Advances in Physics*, 2011, 60, 413-550.
  I. Kruusenberg, N. Alexeyeva, K. Tammeveski, *Carbon*, 2009, 47, 651-658.
- 6 S. P. Jiang, Z. G. Lin, A. C. C. Tseung, *Journal of the Electrochemical Society*, 1990, **137**, 764-769.
- 7 S. P. Jiang, A. C. C. Tseung, *Journal of the Electrochemical Society*, 1991, **138**, 1216-1222.
- 8 B. V. Tilak, C. P. Chen, Journal of Applied Electrochemistry, 1993, 23, 631-640.
- 9 N. Krstajic, in *Encyclopedia of Applied Electrochemistry*, ed. by G. Kreysa, K.-i. Ota, R. Savinell, Springer New York, **2014**, Chap. 403, pp. 1039-1044.
- C. Song, J. Zhang, in *PEM Fuel Cell Electrocatalysts and Catalyst Layers*, ed. by J. Zhang, Springer London, **2008**, Chap. 2, pp. 89-134.
- 11 R. L. Doyle, I. J. Godwin, M. P. Brandon, M. E. G. Lyons, *Physical Chemistry Chemical Physics*, 2013, **15**, 13737-13783.
- Y. Surendranath, D. G. Nocera, in *Progress in Inorganic Chemistry*, John Wiley & Sons, Inc., 2011, pp. 505-560.
- 13 D. K. Bediako, Y. Surendranath, D. G. Nocera, *Journal of the American Chemical Society*, 2013, **135**, 3662-3674.
- 14 Y. Surendranath, M. W. Kanan, D. G. Nocera, *Journal of the American Chemical Society*, 2010, **132**, 16501-16509.