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1. Introduction

Fuel cells or metal–air batteries have attracted extensive interest in the field of electrochemical energy conversion. As a key part of these devices, developing the performances of the oxygen reduction reaction (ORR) is crucial due to the sluggish reaction kinetics on the cathode. Various metal catalysts, especially platinum-group metals (PGMs) have been used for ORR due to their excellent catalytic activities. However, scarcity of resource and inferior durability limit their application. Consequently, reducing the noble metal contents and exploring non-PGM or metal-free catalysts have been attempted in recent years. Among them, metal oxide,^{1–3} carbon materials and their composites^{4–8} seem to be the most attractive ones.

Metal-free non-PGM catalysts, especially nano-carbon materials, such as graphene, carbon nanotubes and other nano-structural carbon materials, have excellent catalytic activities towards ORR. However, inferior long-term stability, that is, their practical performance at high energy density and power density is difficult to maintain on account of the compact restacking that is seriously caused by the large surface energy.⁹ This is different



Jing Li, Jinfu Ma, 🕑 * Hui Lu, Zhilin Sheng, Shaolin Yang and Jiandong Wu ២

Although carbon nanomaterials show good potential as efficient electrocatalysts for oxygen reduction reaction (ORR), their inferior long-term stability due to their high surface energy resulting in compact restacking limits their practical performance. To overcome this issue, here, we design and construct an anti-agglomerating single-walled carbon nanotube (SWNT) catalyst by using poly-3,4-ethylenedioxythiophene (PEDOT) as an upholder. Physical characteristic results indicate that PEDOT effectively fills in the interweaved zone or adheres to the SWNT surface. Furthermore, S atoms can be doped into the lattice and produce more defects. Electrochemical tests show that SWNTs@PEDOT exhibits similar catalytic activities towards ORR to SWNTs, and both of them can realize a quasi-4e ORR pathway. Within a 32 000 s long-term test, the cathodic current of the SWNTs toward ORR gradually decays to 58% of the initial value; in contrast, SWNTs@PEDOT shows excellent stability with several stages of rise, fall, rise to 105% of the initial current. The excellent stability is due to the stable skeleton caused by PEDOT preventing agglomeration of SWNTs. The equilibrium of swelling and shrinkage of PEDOT even lead to an increase and favorable stability of the current. This suggests a practical method to overcome the weakness of agglomeration, thus enhancing the long-term stability for nano-carbon catalysts.

from the degradation mechanism of PGMs and non-PGMs, such as (a) demetallization of metal active sites and (b) Fenton reaction.¹⁰ Qu et al.¹¹ reported a nitrogen-doped graphene catalyst synthesized by chemical vapor deposition of methane in the presence of NH₃, and there was no decay observed in the ORR current after 2 000 000 cycles in alkaline medium. Yu et al.12 developed nitrogen-doped SWNTs, which displayed exceptional long-term stability for two days in acidic medium. At the same time, nanoporous graphitic-C3N4, boron and nitrogen co-doped graphene (BCN) catalysts exhibited high stabilities in O2-saturated 0.1 M KOH solution.¹³ Recently, metal-organic frameworks (MOFs) have attracted great interest as ORR catalysts owing to their various combinations of metal ions and organic ligands, large specific surface areas, and facile synthesis. Zhao et al.14 reported a Co-ZnO@NC/CNT-700 catalyst and explored a slight degradation after 25 000 s toward ORR.

As another kind of metal-free non-PGM catalyst, PEDOT towards ORR has been initially reported by Winther-Jensen, *et al.*¹⁵ in science, 2008; a porous material coated was with PEDOT by a vapor phase-polymerized method, and it acted as an ORR catalyst without material degradation or deterioration in performance for 1500 hours continuous operation. Since then, the theoretical research on the mechanism of oxygen reduction reaction (ORR) catalyzed by PEDOT demonstrated that the remarkable catalytic activity of PEDOT was related to



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School of Materials Science and Engineering, North Minzu University,

Yinchuan 750021, China. E-mail: ma_jinfu@nun.edu.cn

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the formation of polaronic states and provided theoretical proof of the energetically preferable 4e-ORR route.¹⁶ Chen *et al.*¹⁷ also reported a PEDOT:PSS-MWCNT modified carbon black-based gas diffusion electrode and concluded that the π - π interaction between MWCNTs and PEDOT: PSS facilitated 2e-ORR. Zhang *et al.*¹⁸ prepared PEDOT:PSS and rGO composites, then removed a part of the insulating PSS from the surface of PEDOT:PSS/rGO by H₂SO₄ post-treatment, and the ORR performance was equivalent to Pt/C and has excellent stability.

Here, we design a novel method to overcome the weakness of inferior stability of nano-carbon catalysts. Utilizing the stable structural characteristics and favorable ORR catalytic activity of PEDOT to build a stable skeleton structure of SWNTs and prevent agglomeration, we thus enhance the long-term stability of SWNTs.

2. Experimental

2.1. Chemicals

Single-walled carbon nano-tubes (SWNTs, \geq 95 wt%, ϕ < 2 nm, 0.3–5 µm length), 3,4-ethylenedioxythiophene (purity \geq 99%), LiClO₄ (AR, 99.0%), Nafion solution (5%, Dupont), 20 wt% Pt/C, and NaOH (AR and KBH₄) (AR) were purchased from Aladdin and used directly without other modifications.

2.2. Synthesis of electrocatalysts

In order to functionalize SWNTs, 100 mg of SWNT powder was dispersed in 8 mL mixtures of concentrated sulfuric acid and nitric acid with a volume ratio of 3:1, after ultrasonic dispersing for 2 h and stirring for 24 h, and then washed by distilled water and ethanol several times to pH = 7. Finally, the sample was dried at 80 °C in a vacuum oven for 6 h and the functionalized SWNTs (F-SWNTs) were obtained.

Before preparing the working electrodes, the glassy carbon rotating disk electrode (RDE) was polished by an aqueous alumina suspension and washed with deionized water and ethanol. 100 mg of F-SWNTs was mixed with 0.95 mL of ethanol and 0.05 mL of 5% Nafion and then ultrasonically dispersed for 1 h. 5 µL of the suspension was then dropped onto the surface of disk (0.126 cm^2) electrodes. The coated ink was dried using an infrared lamp for 5 min. The SWNT-catalyzed cathode was obtained. In order to prepare PEDOT, 0.1 M LiClO₄ and 1 mM EDOT monomers were dissolved into 50 mL of deionized water. Then, the mixture was ultrasonically dispersed for 0.5 h. PEDOT was prepared by electropolymerization on the surface of the disk electrode directly through a constant potential of 1 V (vs. SCE) for 100 s. Finally, the prepared electrode was rinsed in dichloromethane (CH_2Cl_2) and absolute ethanol to remove the residual EDOT monomer and other unreacted chemicals. Thus, the PEDOT-catalyzed cathode for ORR was obtained. The SWNTs@PEDOT catalyzed cathode was fabricated according to the process described above in turn (Fig. 1).

For comparison, a 20 wt% Pt/C cathode was prepared with a mass loading of 4 mg cm⁻² by the same method as that of the SWNT-catalyzed cathode fabrication.



Fig. 1 Schematic diagram of the synthesis process for SWNTs@PEDOT.

2.3. Physical characterization

The micro morphologies of the samples were studied using field emission scanning electron microscopy (FE-SEM, Zeiss Supra-55) and transmission electron microscopy (Titan G260-300). The exact characterization of the material surface was analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Fisher) with Al K-Alpha (1486.7 eV) operating at 15 kV in high vacuum mode with a pressure of 10^{-8} Pa. The Raman spectrum was recorded using an Invia Raman microscope (Renishaw, England).



Fig. 2 The SEM images of PEDOT (a) and SWNTs-PEDOT (b), TEM images of SWNTs (c) and SWNTs-PEDOT (d), and HAADF of SWNTs (e) and SWNTs-PEDOT (f).

2.4. Electrochemical characterization

Cyclic voltammetry (CV), linear scan voltammetry (LSV) and chronoamperometry (CA) tests were conducted by a three-electrode system controlled by a CHI 760E electrochemical workstation. A Pt plate, Hg/HgO (1 M KOH), and the bare or functionalized rotating disk electrode (RDE) carbon disk with a surface area of 0.1256 cm² were used as auxiliary, reference and working electrodes, respectively. The reference electrode was replaced by the SCE electrode when electro-polymerization was carried out for PEDOT. The potential of the HgO/Hg reference electrode was corrected with the reversible hydrogen electrode (RHE), in 0.1 M KOH, *E vs.* RHE = 0.059pH + 0.098. Electrochemical surface area (ECSA) of the catalysts was estimated by using the double-layer capacitance in the non-Faraday area at scan rates of 10, 20, 30, 40, 50 mV s⁻¹, and the ECSA (cm²) was calculated according eqn (1),¹⁴

$$ECSA = \frac{C_{DL}}{C_s} = \frac{i_c}{vC_s}$$
(1)

The double layer capacitance $(C_{\rm dl})$ was estimated by plotting $\Delta j(j_{\rm a} - j_{\rm c})$ at 0.95 V vs. RHE against the scan rate.

CV and LSV were performed in O₂-saturated 0.1 M aqueous KOH solution at a scan rate of 50 mV s⁻¹. And LSV curves were

measured at different rotating rates (600–3200 rpm) with a sweep rate of 50 mV s⁻¹. The number of electron transfer toward ORR was calculated from the slope of $j_d^{-1} \sim w^{1/2}$ according to the Koutecky–Levich (K–L) equation as follows,¹⁹

$$\frac{1}{j} = \frac{1}{j_{\rm k}} + \frac{1}{j_{\rm d}} = \frac{1}{j_{\rm k}} + \frac{1}{Bw^{1/2}} \tag{2}$$

$$B = 0.2nFAC_{O_2}D_{O_2}^{2/3}v^{-1/6}$$
(3)

where *j* is the measured current density; j_k and j_d are the kineticand diffusion-limiting current densities; *n* is the electron transfer number; *F* is the Faraday constant ($F = 96485 \text{ Cmol}^{-1}$); *A* is the geometric area of the electrode (0.1256 cm²); *k* is the electron transfer rate constant, C_{O_2} is the bulk concentration of O_2 ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$); D_{O_2} is the diffusion coefficient of O_2 in 0.1 M KOH solution ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$); ν is the kinematic viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$), and *w* is the electrode rotating rate (rpm).

The stability tests were carried out at 0.7 V vs. RHE in O₂-saturated 0.1 M KOH (ω = 1225 rpm) by CA. During the stability evaluation, 2 M methanol or 2 mM KBH₄ was injected into O₂-saturated 0.1 M KOH. Meanwhile, a commercial 20 wt%



Fig. 3 (a) XPS spectrum of PEDOT and SWNTs@PEDOT. The corresponding high resolution XPS spectra and fitting lines of (b) C1s, (c) O1s and (d) S2p regions in PEDOT and SWNTs@PEDOT.

Pt/C catalyst was measured as a contrast. All the tests were carried in 0.1 M KOH at ambient temperature.

3. Results and discussion

Fig. 2 shows the SEM and TEM images of the as-synthesized catalysts. Fig. 2a exhibits an irregular flake structure. PEDOT has been synthesized successfully by electro-polymerization in LiClO₄ aqueous solution and many acicular crystals distributed on the surface, which is unlike the microstructure of PEDOT synthesized by the same method on fluorinated tin oxide (FTO) glass in our previous work,²⁰ indicating that the polymerization and growth of PEDOT are dramatically affected by the substrate. On the SWNT-modified glassy carbon surface, PEDOT displayed a regular linear polymer coating (Fig. 2b), which would be beneficial to enhance the electro-catalytic activity for ORR. Fig. 2c and d display the TEM images of SWNTs and SWNTs@PEDOT, with Nafion gel only distributed in the lapping zone of the SWNTs (Fig. 2c), and the distribution characteristics of S element from Nafion shown in the HAADF image (Fig. 2e) also provide proof. By comparison, for SWNTs@PEDOT, PEDOT attached to the interweaved network of SWNTs (Fig. 2d), and the HAADF image (Fig. 2f) shows that more S element distributes not only on the surface of the SWNTs (S from Nafion and PEDOT) but also in other zones (S from PEDOT), and Fig. S1 (ESI⁺) also shows the structural characters described above.

In order to investigate the surface elemental composition and electronic configuration of the catalyst, XPS was utilized. The survey scan (Fig. 3a) shows the presence of C1s, O1s, and S2p. Among the detected elements, F and some S element in the SWNTs resulted from the Nafion solution. The high-resolution C1s XPS spectra (Fig. 3b) of PEDOT can be deconvoluted into three peaks with binding energies located at 284.5 eV, 285.1 eV and 286.4 eV, associated with C=C, C-S and C-O.^{20,21} The C=C (284.7 eV), C-S (285.0 eV) and C-O (286.2) peaks can be deconvoluted for SWNTs/PEDOT²² in the same way. Furthermore, C=O-C (289.2 eV) and C-F (291.8 eV)²³ peaks can also be observed with the F element resulting from the Nafion solution. The O1s spectra (Fig. 3c) have asymmetric peaks for PEDOT and SWNTs-PEDOT, which were deconvoluted with two peaks assigned to 532.1 \pm 0.1 eV for C–O–C/O=C bonds and 533.4 \pm 0.1 eV for O-C,²⁴ demonstrating that the SWNTs were functionalized successfully. The higher binding energy of 535.4 eV for SWNTs@ PEDOT can be attributed to adsorbed oxygen contaminants.^{24,25} In the high-resolution S2p spectrum (Fig. 3d) of PEDOT and SWNTs@PEDOT, the peaks at 163.9 eV and 165.1 eV are in agreement with the $S2p_{3/2}$ and $S2p_{1/2}$ positions associated with C–S–C bonds.^{21,26} One shakeup satellite peak at 168.5 eV of S2p in PEDOT was also found that is assigned to a higher oxidation state of S.27 Again, SWNT@PEDOT exhibits two prominent satellite peaks at 168.5 eV and 169.7 eV that are assigned to the surface sulfur species of higher oxidation states in C-SO_x-C bonds from PEDOT and Nafion solution, respectively; the peak of 168.5 eV of S2p for SWNTs@PEDOT remarkably grew relative to PEDOT, indicating that S (from the integral area) of PEDOT was doped into the carbon skeletons of the SWNTs, and this is very useful as S doped in carbon materials is known as one of the most probable active sites in ORR.²⁶ Consequently, the electrochemical ability is potentially enhanced due to the S doping. All the fitting data of binding energies and their corresponding bonds are listed in Table 1.



Fig. 4 Raman spectra of SWNTs and SWNTs@PEDOT.



 Table 1
 Results obtained from fitting of XPS C1s, O1s and S2p spectra of

 PEDOT and SWNTs-PEDOT

	PEDOT	SWNTs-PEDOT	Assignment
	BE/eV	BE/eV	
C1s	284.5	284.6	C=C
	285.1	285.0	C–S
	286.4	286.2	C-O
		289.1	O=C-O
		291.8	C-F
O1s	532.2	532.0	C-O-C/O=C
	533.3	533.5	O-C
		535.4	O _{ads}
S2p	163.8	164.0	C-S-C
	165.0	165.3	C-S-C
	168.5	168.5	$C-SO_x-C$
		169.7	$C-SO_x-C$

Fig. 5 The CV curves of various catalysts toward ORR (scan rate: 0.05 V $s^{-1},$ O2- or N2-saturated 0.1 M KOH solution).

Fig. 4 shows the Raman spectra of SWNTs and SWNTs(a) PEDOT. For the SWNTs, there are typically three characteristic peaks containing a defect-related D band at 1356 cm⁻¹ and G band at 1591 cm⁻¹ attributed to the vibration of the sp²-hybridized carbon atoms, and the second order of the D band (2D band) at 2672 cm⁻¹.²⁸ The intensity ratio of D band to G band (I_D/I_G) is often used to indicate the defect level in carbon materials. The I_D/I_G values of 0.14 for the pure SWNTs and 0.28 for SWNTs(a)PEDOT suggest more sonication induced basal plane defects and/or edge defects.

The CV tests of the as-prepared samples were performed in N_2 - and O_2 -saturated 0.1 M KOH solutions at a scan rate of

50 mV s⁻¹. As shown in Fig. 5, no cathode reduction peak appears with the N₂-saturated solution, indicating that this catalyst is inactive in N₂. An obvious cathode peak appears, and the onset potential and peak potential of PEDOT in O₂-saturated 0.1 M KOH aqueous solution are ~0.65 V and 0.51 V (0.55 mA cm⁻²), respectively. However, no cathodic polarization current or peaks appear under the condition of N₂-saturation, indicating that PEDOT has catalytic ability towards ORR. In contrast, the SWNT and SWNTs@PEDOT catalyzed electrodes display excellent properties for ORR; the corresponding onset potential is 0.75 and 0.8 V, and the peak potentials are 0.67 and 0.71 V with a similar peak current



Fig. 6 The LSV curves of PEDOT (a), SWNT (c), and SWNTs@PEDOT (e) catalysts toward ORR with various RDE rotating rates and a corresponding slope of $j_d \sim w^{1/2}$ of PEDOT (b), SWNT (d), and SWNTs@PEDOT (f) catalysts (scan rate: 0.05 V s⁻¹, O₂-saturated 0.1 M KOH solution).

density (~ -0.85 mA cm⁻²), respectively. The more positive onset potential of SWNTs@PEDOT indicates a higher catalytic activity for ORR.

The LSV curves of various catalysts in the rotating rate of RDE range of 600-3200 rpm at 50 mV s⁻¹ are presented in Fig. 6(a, c and e); the current densities gradually increase with increasing disk rotating rate. The number of electron transfer toward ORR is calculated from the slope of $i_d^{-1} \sim w^{1/2}$ according to eqn (2) and (3), and the K-L plots are displayed in Fig. 6(b, d and f). For PEDOT, n is determined to be ~2.2 ranging from -0.10 ~ -0.30 V of the limit current density (j_d) region. Within the j_d region of 0.50-0.40 V, SWNTs and SWNTs@PEDOT toward ORR have very similar *n* values greater than 3. Moreover, the potentials of the i_d region are more positive, which would be beneficial to enhance the work voltage and power density for electrochemical devices. This indicates that the two catalysts have superior catalytic activities toward ORR in contrast to the PEDOT and SWNT catalysts that display a slightly larger *n* value of 3.41 than that of SWNTs@PEDOT (3.13) at 0.30 V.

The catalytic activities were also explored by using Tafel plots within the mixed kinetic-diffusion (j_k) region of LSV curves at 1600 rpm, as shown in Fig. 7a; the slopes of the Tafel plots of PEDOT, SWNTs and SWNTs@PEDOT toward ORR are 195.6, 142.4 and 126.9 mV dec⁻¹, respectively, which display that PEDOT has an inferior catalytic activity due to great polarization while SWNTs@PEDOT exhibits an ideal catalytic activity with a lower slope value, which is close to a general Tafel slope of 120 mV dec⁻¹, indicating the fast electron transfer ratedetermining step^{19,22} of SWNTs@PEDOT toward ORR. Thus, this result demonstrated that the fast electron exchange is the rate-determining step on SWNTs@PEDOT. To further evaluate the different activities of the catalysts, ECSA was studied to characterize the amount of active sites exposed to the electrolyte. According to the CVs within the non-faradaic area (Fig. S2, ESI⁺), the $\Delta j \sim \nu$ relation curves are shown in Fig. 7b and the $C_{\rm dl}$ values calculated in terms of the slopes of $\Delta j \sim v$ for PEDOT, SWNTs and SWNTs@PEDOT are 0.64, 0.93 and 1.16 mF with a trend of PEDOT < SWNTs < SWNTs@PEDOT, which is consistent with

that of the ORR catalytic activities. This is perhaps due to the π - π conjugative effects¹⁷ of SWNTs and PEDOT that enhance the electron conductivity and provide the synergetic promotional effect for ORR.

The methanol tolerances of PEDOT, SWNTs, SWNTs@PEDOT and Pt/C were determined from chronoamperometric measurements performed in O2-saturated 0.1 M KOH solution. As shown in Fig. 8a, within 1000 s short-term tests, all catalysts exhibited a sudden fluctuation when injecting 2 M methanol at ~ 300 s. With the increase of time, the current of PEDOT, SWNTs and SWNTs@PEDOT quickly returned to the initial state, but Pt/C exhibits a drop of -1000% of initial current with a gradual recovery, indicating that PEDOT, SWNTs and SWNTs@PEDOT have favorable anti-methanol tolerance. As shown in Fig. S3 (ESI[†]), when 2 mM KBH₄ was added into 0.1 M KOH during the tests at 500 s, PEDOT and SWNTs@PEDOT retained good borohydride tolerance, while SWNTs and Pt/C did not. The anodic current on the SWNTs confirmed that they can also catalyze BOR. As a comparison, a sudden and large anodic current on Pt/C indicated that Pt/C has a good catalytic activity for borohydride oxidation reaction (BOR) with very poor selectivity, which agreed with ref. 29. In contrast, the Pt/C electrode exhibits a gradual decrease with more current loss and a lower relative current (\sim 43.9%). Thus, the tests show that the SWNTs@PEDOT catalyst has great anti-poisoning effects in KBH₄ and methanol tolerance, that is, PEDOT was beneficial for the enhancement of the electro-catalytic activity and selectivity of SWNTs in ORR, and SWNTs@PEDOT has great potential for application in alkaline direct borohydride fuel cells (DBFCs) and direct methanol fuel cells (DMFCs).

For nano-structured carbon materials, a high surface energy can result in aggregation, which limits ion transport thus causing inferior long-term stability. Long-term tests for 32 000 s of SWNT and SWNTs@PEDOT catalysts were carried in O₂-saturated 0.1 M KOH solution at a constant potential of 0.7 V (ν s. RHE). As displayed in Fig. 8b, the current of the SWNTs toward ORR gradually decays to only 58% of the initial value at 32 000 s, mainly because the agglomeration conductance of carbon nanotubes limited the



Fig. 7 (a) The Tafel plots within the mixed kinetic-diffusion (j_k) region of LSV curves at 1600 rpm; (b) the anode and cathode current variance ($\Delta j = j_a - j_c$) in the non-faradaic region with scan rates of 10, 20, 30, 40, and 50 mV s⁻¹ of PEDOT, SWNT and SWNTs@PEDOT catalysts.



Fig. 8 (a) The anti-methanol tolerance tests of various catalysts (inset: enlarged view of $j/j_0 \sim$ time of various catalysts except Pt/C); (b) the long-term stability of SWNTs and SWNTs@PEDOT (constant potential: 0.7 V vs. RHE, O₂-saturated 0.1 M KOH solution, rotating rate: 1225 rpm).

migration of electrons, resulting in poor long-term stability. However, that of SWNTs@PEDOT shows excellent stability with several stages of rise, fall, rise to 105% of the initial current and then stability. The excellent stability of SWNTs@PEDOT is due to the stable skeleton of PEDOT that can effectively prevent the aggregation of SWNTs; in addition, the swelling and shrinkage of PEDOT result in the fluctuation of current and its equilibrium leads to increased and favorable stability of current.

4. Conclusion

A highly selective and long-term stable ORR catalyst of SWNTs@ PEDOT was prepared by electro-polymerization on surface SWNTs directly. Several physical characterization and electrochemical techniques were carried to determine the catalytic effects of PEDOT, SWNTs and SWNTs@PEDOT toward ORR in alkaline medium. The results indicated that PEDOT attached to the interweaved network of SWNTs and trace amounts of S from PEDOT were doped into the SWNTs to increase the ECSA and create structural defects; coupled with the π - π conjugative effects of SWNTs and PEDOT, the SWNTs@PEDOT exhibited similar catalytic activities to those of the SWNTs. Furthermore, SWNTs@PEDOT has a great antipoisoning effect in KBH4 and methanol tolerance and excellent long-term stability in alkaline medium, that is, PEDOT is beneficial for the enhancement of the electro-catalytic activity, selectivity and stability of SWNTs toward ORR, and SWNTs@PEDOT has great potential for applications in DBFCs and DMFCs.

Conflicts of interest

There are no conflicts to declare.

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