

Improved Oxygen Reduction Activity on PEDOT Via Electrolymerisation In Ionic Liquid

Jinfu Ma^{1,*}, Tong Xue¹, Zhongli Zou¹, Beiping Wang¹, Min Luo²

¹School of Material Science and Engineering, Beifang University of Nationalities, Yinchuan 750021, PR China

²College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, PR China

*E-mail: jinfu_ma@163.com

Received: 20 February 2015 / Accepted: 23 February 2015 / Published: 28 April 2015

It has been demonstrated that the electrolyte of electropolymerisation of Poly(3,4-ethylenedioxythiophene)(PEDOT) have a significant influence on the electro-catalytic activity for reduction of oxygen. It is notable that PEDOT-modified electrode via electropolymerisation in ionic liquid (GC/PEDOTIL) possesses remarkable electrocatalytic properties for oxygen reduction reaction (ORR) as compared with the electrode obtained from aqueous solution (GC/PEDOTaq). The exchange current densities have been achieved to be 86:1, it indicates the excellent catalytic properties of GC/PEDOTIL. Nevertheless, the number of electron transferred by per O₂ molecule(n) calculated from the slope of the Koutecky-Levich plots [J^{-1} vs $\omega^{-1/2}$] is to be 2, it means the ORR proceeds via the 2-electron pathway only in alkaline media on PEDOT decorated electrode.

Keywords: Oxygen reduction reaction (ORR), Poly(3,4-ethylenedioxythiophene) (PEDOT), Ionic liquid, Electron-transfer mechanism

1. INTRODUCTION

The air electrode, which reduces oxygen (O₂), is a critical component in energy generation and storage applications such as fuel cells and metal/air batteries [1-4]. The sluggish kinetics of the cathodic oxygen reduction reaction (ORR) significantly limits the efficiency of electrochemical energy conversion in fuel cells and metal/air batteries [5]. The highest current densities are achieved by using platinum (Pt) as the catalyst, however, the usage of Pt is limited by its cost and scarcity. The activity of Pt particles in composite electrodes could be reduced by agglomeration or combining with carbon monoxide (CO) [1]. Therefore, non-precious metal catalysts [1,4,6-11] and enzymatic electro catalysts[12] have been devoted to reduce or substitute Pt usage. With the development of new type carbon materials, especially carbon nanotube and graphene, metal-free catalysts have commanded

researchers' great interest. Du *et al.* pointed out that "the metal - free carbon nanomaterials become more active than the metal catalysts and last longer" [13]. As compared with Pt catalyst, metal-free catalyst has no CO poisoning and fuel penetration effect, and has long-term operation stability and low price. Recently, the N, P, B, S doped carbon materials [13-29] and functional carbon materials [30] have been focused by researchers. For example, the vertically aligned nitrogen containing carbon nanotubes (VA-NCNTs) fuel cell cathodes have been demonstrated with superior oxygen-reduction activities, operational stability, crossover effects tolerance, and CO poisoning resistance [3].

An air electrode based on a porous material coated with poly(3,4-ethylenedioxythiophene) (PEDOT), which acts as an O₂ reduction catalyst without material degradation or deterioration, has been developed by Winther-Jensen *et al.* It could work for 1500 hours. In addition, PEDOT electrode is inert to CO^[1]. In latest research [31], it has been found that the polymerization method to prepare the conducting polymer PEDOT have influenced the electro-catalytic pathway of oxygen reduction significantly .

Here, based on the previous research [32], aims to demonstrated the influence on improve oxygen reduction activity of Poly(3,4-ethylenedioxythiophene)(PEDOT) electropolymerisation media the PEDOT electropolymerised in ionic liquid and ORR catalytic mechanism has been investigated.

2. EXPERIMENTAL SECTION

All chemicals were reagent grade, used without further purification. The monomer, EDOT has been obtained from Aldrich (Purity:97%). The ionic liquid 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ([EMIm][NTf₂]) (Purity:99%) was from Lanzhou institute of chemical physics, China.

The cyclic voltammograms (CV), galvanostatic line sweep voltammograms (LSV) and Tafel curves were carried out in a conventional three-electrode arrangement using a computer controlled CHI760E Electrochemical Workstation (CH Instrument, Inc. USA). The rotating disk electrodes (RDE-3A, BAS inc. Japan) glassy carbon electrode (GCE, $\Phi=0.4$ cm) served as the working electrode. Ag/AgCl(3 M KCl) and Hg/HgO(6 M KOH) electrodes as reference electrodes used in electropolymerisation and ORR test, respectively. A Pt wire as a counter electrode. The reference electrodes were connected to the main body of the cell through a Luggin capillary, whose end was centered on the working electrode and positioned closed to the electrode surface.

Using field emission scanning electron microscope (FE-SEM, JEOL-7500F, Japan), the morphology information of the PEDOT was characterized.

3. RESULTS AND DISCUSSION

3.1 Electropolymerisation of EDOT in different media

The applied potential is one of the most significant parameters in electropolymerisation process. Therefore, establishing the potential range to synthesize polymer films with satisfactory value is conditioned by the fact that the polymer could not be overoxidised.

3,4-Ethylenedioxythiophene is poorly soluble in aqueous solution, hence it has been used in relatively low concentrations to guarantee homogeneous media. After the solution of 0.01 M EDOT+0.1 M Na₂SO₄ stood for 24 h, the color of the mixture solution would convert to yellow. It indicates that the oligomer has been generated.

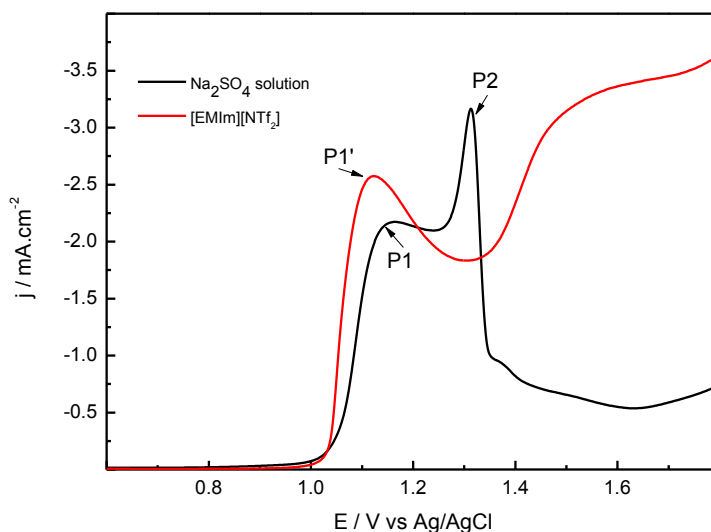


Figure 1. LSV of EDOT on GC electrode in 0.1 M Na₂SO₄ aqueous solution (black) and in ionic liquid [EMIm][NTf₂] (red) media containing 0.01 M EDOT at 10 mV/s.

Figure.1(black curve) shows the linear sweep voltammogram of 0.01M EDOT aqueous solution containing 0.1 M Na₂SO₄ at sweep rate of 10 mVs⁻¹. Two oxidation peaks, P1 and P2, locate at +1.15 and 1.31 V, respectively. The two peak potential values are in agreement with previously reported data [32, 33]. According to data analysis, the first peak (P1) is related to the oxidation of monomer, which adsorbed on or free from the electrode surface [33]. The second peak (P2) is related to the oxidation of EDOT species diffused to the electrode closely, or the overoxidation of the PEDOT film as enough amount of polymer deposited on the electrode [33]. Therefore, as shown in Fig.1, potential of +1.15 V was been selected for electropolymerisation process (GC/PEDOTaq).

EDOT can easily dissolve in [EMIm][NTf₂]. Therefore, it is unnecessary to leave the solution on standing before use. As shown in the Figure.1 (red curve), the peak potential (P1') related to the oxidation of monomer shifts negatively to 1.1 V, and the potential of overoxidation peak shifts positively. It indicates the electropolymerisation process is easier as comparing with the one dissolved in ionic liquid, and overoxidation will be limited. The existence of ionic liquid could help to obtain high quality of conductive polymer PEDOT. As a result, 1.1 V was applied as electropolymerisation potential (GC/PEDOTIL).

The GC/PEDOTaq and GC/PEDOTIL were prepared by potentiostatic polymerization for 200 seconds, and then soaked in dichloromethane(CH₂Cl₂) in 24 hours to remove residual EDOT monomer and [EMIm][NTf₂]. Before electrochemistry test, the electrodes were left to stand in 0.1 M KOH solution for 8 hours.

3.2 Characterization of morphology

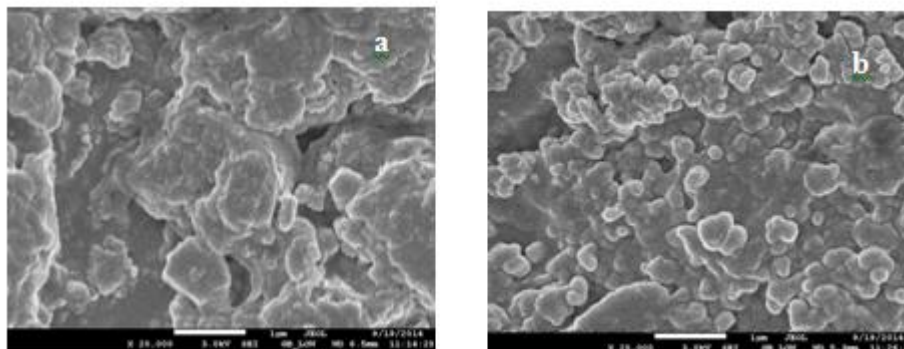


Figure 2. FE-SEM images of PEDOT from electropolymerisation in (a) aqueous solution and (b) ionic liquid ([EMIm][NTf₂])

The FE-SEM micrographs of GC/PEDOTaq and GC/PEDOTIL are shown in Figure 2. From the images, the structural distribution the PEDOT synthesized in ionic liquid (Figure 2b) is even and particle size are mainly distributed in 100-200 nm. By contrast, no uniform particles were observed when the polymerization was carried out aqueous solution (Figure 2a), this confirms that the ionic liquid plays a vital role in preventing particle aggregation during synthesis.

3.3 Electrocatalytic behavior of PEDOT for ORR

3.3.1 Cyclic voltammetry(CV)

The cyclic voltammograms (CVs) of oxygen reduction in O₂-or N₂-saturated 0.1 M KOH solutions at different electrodes are shown in Figure 3A. For the PEDOT-modified GCE in aqueous solutions, the ORR peaks could be observed clearly in the O₂-saturated, but not N₂-saturated 0.1M KOH solution.

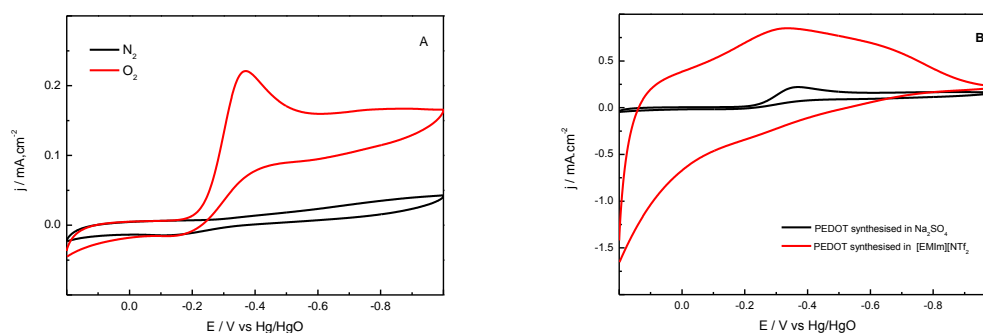


Figure 3. Cyclic voltammograms of ORR on various electrocatalysts in O₂ or N₂ saturated 0.1 M KOH solution. (A) GC/PEDOTaq in N₂(black) and O₂(red) saturated solution. (B) GC/PEDOTaq(black) and GC/PEDOTIL(red) in O₂ saturated solution.

The onset potential of ORR is -0.2 V (versus Hg/HgO) with a single cathodic reduction peak of around -0.37 V (versus Hg/HgO). It indicates PEDOT has a good electrochemical catalytic effect for ORR in the alkaline solution that has been reported by Winther-Jensen [1] and our group [32]. By contrast, the CV of ORR catalyzed by PEDOT-modified GCE in ionic liquid has apparent changes. The onset potential of ORR shifts negatively and the reduction peak shifts positively to around 0.3 V, with a concomitant increase in the peak current density (Figure 3B). It indicates the ORR electrocatalytic activity of PEDOT has a significant enhancement in ionic liquid media. As reported by Kerr et al. [31], the polymerization method used to prepare the conducting polymer PEDOT has a significant influence on the electro-catalytic pathway for the reduction of oxygen.

Combining the FE-SEM images (Figure 2), the uniform structure distribution and smaller particle size of GCE/PEDOTIL provide greater specific surface area and catalytic active sites for ORR.

3.3.2 Tafel analysis

In order to demonstrate the improved ORR activity on PEDOT via electropolymerisation in ionic liquid further, the Tafel curves have been carried out. Exchange current densities reflect intrinsic rates of electron transfer between analyte and the electrode. The intrinsic rates provide insights into the structure of electrode materials and bonding in the electrolyte and the electrode.

An electrochemical reaction under kinetic control obeys the Butler-Volmer equation, which relates the exponential dependence of current to the deviation of voltage from the open circuit potential. Therefore, by potentiostatically measuring the dependence and plotting the logarithm of current density (i) vs. potential (V), it is possible to extract the reaction kinetic parameters, such as exchange current density [34].

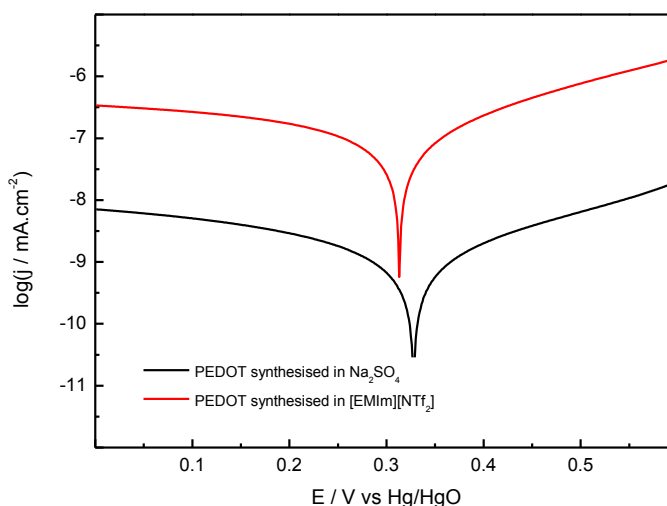


Figure 4. Tafel curves of GC/PEDOTaq(black) and GC/PEDOTIL (red) electrodes in O_2 -saturated 0.1 M KOH solution at 0.001 $V \cdot s^{-1}$

As shown in Figure 4, the cathodic/anodic branches were obtained in the O_2 -saturated 0.1 M KOH solutions at scan rate of 0.001 $V \cdot s^{-1}$. It is notable that the equilibrium potential of the

GC/PEDOTIL electrode had 16 mV shifts to negative potential and significantly larger current compared to GC/PEDOTAq electrode. Through a linear fit by excluding larger overpotentials (larger than 200 mV), exchange current densities of $1.01 \times 10^{-6} \text{ A}\cdot\text{cm}^{-2}$ and $8.57 \times 10^{-5} \text{ A}\cdot\text{cm}^{-2}$ were obtained from the point of intersections, respectively. The ratio of 86:1 on exchange current densities indicates the excellent catalytic properties of GC/PEDOTIL.

3.3.3 Electro-transfer mechanism

RDE voltammetry measurements were also carried out to gain further insight on the ORR performance of the GC/PEDOTIL electrode.

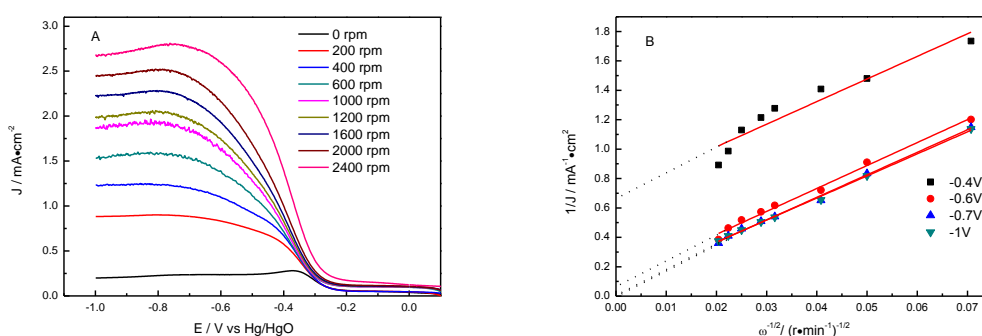


Figure 5. LSV of GC/PEDOTIL on RDE at different rotating rates (0 to 2400 rpm) in O_2 -saturated 0.1 M KOH solution (A) and corresponding Koutecky-Levich plots at different potentials (B).

Figure 5A shows RDE I - V curves at different rotation rates for GC/PEDOTIL electrode. It is clearly shown, the limiting current density increases with rotation rate increasing. The transferred electron number per oxygen molecule involved in the oxygen reduction was determined by the Koutecky-Levich equation given below [34,35]:

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{B\omega^{0.5}}$$

where J_k is the kinetic current and ω is the electrode rotating rate. B is determined from the slope of K-L plots (Figure 5B) based on Levich equation as follows [35]:

$$B = 0.2nF(D_{\text{O}_2})^{2/3}\nu^{-1/6}C_{\text{O}_2}$$

Where n is transferred electron number, D_{O_2} is well-established values for the diffusion coefficient ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν is kinematic viscosity ($0.01 \text{ cm}^2 \text{ s}^{-1}$), C_{O_2} is solubility limit ($= 1.2 \times 10^{-6} \text{ mol dm}^{-3}$) of gaseous oxygen in KOH (aq, 0.1 mol dm^{-3}) at 298 K, and F is the Faraday constant ($96485 \text{ C} \cdot \text{mol}^{-1}$). The constant 0.2 is adopted when the unit of rotation speed is in rpm. It was assumed that the active area of each film is equal to the geometric area (0.1256 cm^2).

As shown in Figure 5B, a linear relationship between J^{-1} and $\omega^{-0.5}$ was observed for the GC/PEDOTIL electrode at -0.4 V , -0.6 V , -0.7 V and -1.0 V . All fitting lines parallel to each other, and two electrons ($2e^-$) transfer were calculated from the slope of the K-L plots with 1 mol O_2 reaction.

It indicates ORR at the GC/PEDOTIL electrode is only via the classical two-electron process. The presented result is in good agreement with the one that literature reported [31]. The reversely extended fitting lines at higher overpotentials (-0.7 V and -1.0 V) pass through the zero point. It indicates the electrode reaction is a fully diffusion-controlled process whereas a dynamics and diffusion mixed controlled process carries out at lower overpotentials (-0.4 V and -0.6 V).

3.3.4 Stability test

The stability and the methanol tolerance are important issues for cathode materials in low-temperature fuel cells. Pt-based catalysts could be poisoned easily during methanol oxidation procedure. The durability of GCE/PEDOTIL was evaluated by the chronoamperometric response under constant cathodic voltage of -0.4 V.

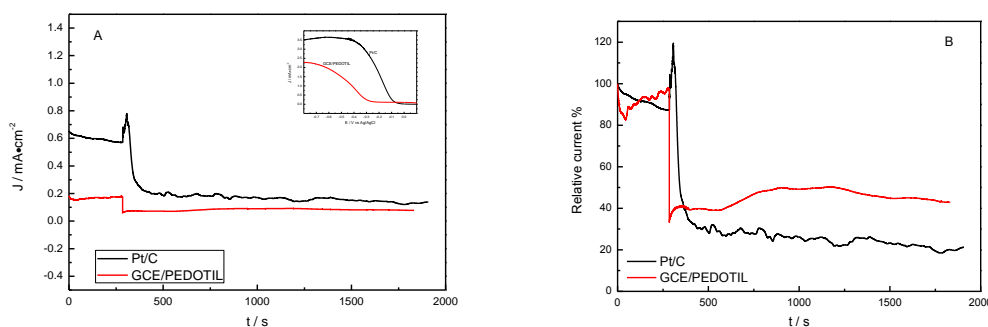


Figure 6. Chronoamperometric responses of GCE/PEDOTIL(red) and Pt/C(black)-modified GC electrodes with 3 M methanol added at around 300 s at -0.40 V in an O₂-saturated 0.1 M KOH solution. (Inset- LSVs of GCE/PEDOTIL(red) and Pt/C(black)-modified GC electrodes at 1600 rpm in O₂-saturated 0.1 M KOH solution)

As shown in Figure 6, linear scan voltametrys (LSVs) curves (inset) of GCE/PEDOTIL and Pt/C-modified GC electrodes have been tested at 1600 rpm. It has been shown that the catalytic ability for ORR of Pt/C is still better than that of GCE/PEDOTIL, remarkably. As shown in Figure 6A, the original cathodic ORR current of GCE/PEDOTIL under -0.4 V had no significant change after the scheduled addition of methanol into the electrolyte solution (the resulting methanol concentration is 3 M), while the current of Pt/C shifted from a cathodic current to a reversed anodic current in a very short time after methanol addition, it means the dominated oxygen reduction reaction converted to the methanol oxidation reaction. The relative current of GCE/PEDOTIL could be increased after ca. 150 s. After addition of methanol, the catalysts were held at -0.40 V for 1800 s in an O₂-saturated 0.1 M KOH solution. From Figure 6B, it can be seen that the chronoamperometric response of GCE/PEDOTIL exhibits slower attenuation as compared with that of the Pt/C electrode. The relative current of GCE/PEDOTIL persisted 50% at 1800 s, by contrast, the current loss of Pt/C approximately reached to 80% at 1800 s.

It also can be seen from Figure 5A, after addition of methanol, the cathodic current of GCE/PEDOTIL electrode increases gradually after a sudden drop, while current of Pt/C electrode continues to decline. It has been investigated that the Pt electrode has been poisoned by carbon monoxide (CO) during methanol oxidation while PEDOT electrode could not be [36]. With the methanol concentration decreasing, the cathodic current for ORR of GCE/PEDOTIL electrode increase gradually.

As the results, GCE/PEDOTIL exhibits high stability and has a good ability for avoiding CO poisoning from methanol oxidation. It has been demonstrated that GCE/PEDOTIL has potential usage in direct methanol and alkaline fuel cells.

4. CONCLUSIONS

In summary, this study has demonstrated that the electrolyte of electropolymerisation of PEDOT have a significant influence on the electro-catalytic activity for reduction of oxygen. It is notable that PEDOT-modified electrode via electropolymerisation in ionic liquid ([EMIm][NTf₂]) possesses remarkable electrocatalytic properties for ORR. From the slope of the Koutecky-Levich plots, it could be found that the ORR on PEDOT prepared electrochemically proceeds via the 2-electron pathway only in alkaline media. The GCE/PEDOTIL exhibits high stability and has a good ability for avoiding CO poisoning from methanol oxidation. The SEM images show that GC/PEDOTIL provides a porous electrode with high porosity, high specific surface, high gas / liquid / solid three phase boundary reaction zone (Figure 3b), which accelerates the gas phase reaction in the liquid phase mass transfer process; significantly improve the cathodic reaction rate. The mechanism of PEDOT electropolymerisation in ionic liquid will be investigated in further research.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of Ningxia Hui Autonomous Region, China (No. NZ14097) and the National Natural Science Foundation of China (Grant No 21361020).

References

1. B. Winther-Jensen, O. Winther-Jensen, M. Forsyth and D. R. MacFarlane, *Science*, 2008, 321 (2008) 671
2. R. Bashyam, P. Zelenay, *Nature*, 443 (2006) 63
3. K. Gong, F. Du, Z. Xia and M. Durstock, L. Dai, *Science*, 323 (2009) 760
4. M. Lefèvre, E. Proietti F. Jaouen and J-P. Dodelet, *Science*, 324 (2009) 71
5. Y. Zheng, Y. Jiao, J. Chen J. Liu, J. Liang, A. Du. W. Zhang, Z. Zhu, S.C. Smith, M. Jaroniec. G. Q. Lu and S. Qiao, *J. Am. Chem. Soc.* 133 (2011) 20116
6. Z. Yang, X. Zhou, H. Nie, Z. Yao and S. Huang, *ACS Applied Materials & Interfaces*. 3 (2011) 2601
7. K. Lee, L. Zhang, H. Liu, R. Hui, Z. Shi and J. Zhang, *Electrochim.Acta.*, 54 (2009) 4704
8. Z. Shi, H. Liu, K. Lee, E. Dy, J. Chlistunoff, M. Blair, P. Zelenay, J. Zhang and Z. Liu, *J. Phys.*

- Chem. C.*, 115 (2011) 16672
9. R. Chen, H. Li, D. Chu, G. Wang and G. Richard, *J. Phys. Chem. C*, 113 (2009) 20689
 10. S. Zhang, X. Ren and J. Read, *Electrochimica Acta.*, 56 (2011) 4544
 11. Z. Wen, S. Ci, F. Zhang, X. Feng, S. Cui, S. Mao, S. Luo, Z. He and J. Chen, *Adv. Mater.*, 24 (2012) 1399
 12. J. P. Collman, N. K. Devaraj, R. A. Decreau, Y. Yang, Y. L. Yan, W. Ebina, T. A. Eberspacher and C. E. D. Chidsey, *Science*, 315 (2007) 1565
 13. D. Yu, E. Nagelli, F. Du and L. Dai, *J. Phys. Chem. Lett.*, 1 (2010) 2165
 14. R. Liu, D. Wu, X. Feng and K. Müllen, *Angew. Chem. Int. Ed.*, 49 (2010) 2565
 15. S. Yang, X. Feng, X. Wang and K. Müllen, *Angew. Chem. Int. Ed.*, 50 (2011) 5339
 16. D. J. Wiggins-Camacho, K. J. Stevenson, *J. Phys. Chem. C*, 115:(2011) 20002
 17. T. Chen, Z. Cai, Z. Yang, L. Li, X. Sun, T. Huang, A. Yu, H. G. Kia and H. Peng, *Adv. Mater.* 23 (2011) 4620
 18. L. Zhang, Z. Xia, *J. Phys. Chem. C*, 115 (2011) 11170
 19. Z. W. Liu, F. Peng, H. J. Wang, H. Yu, W. X. Zheng and J. Yang, *Angew. Chem. Int. Ed.*, 50 (2011) 3257
 20. L. Yang, S. Jiang, Y. Zhao, L. Zhu, S. Chen, X. Wang, Q. Wu, J. Ma, Y. Ma and Z. Hu, *Angew. Chem. Int. Ed.*, 50 (2011) 1
 21. S. Wang, E. Iyyamperumal, A. Roy, Y. Xue, D. Yu and L. Dai, *Angew. Chem.*, 123 (2011) 11960
 22. Y. Zheng, Y. Jiao, J. Chen, J. Liu, J. Liang, A. Du, W. Zhang, Z. Zhu, S. C. Smith, M. Jaroniec, G. Q. (Max) Lu and S. Z. Qiao, *J. Am. Chem. Soc.*, 133 (2011) 20116
 23. S. Lyth, Y. Nabaie, S. Moriya, S. Kuroki, M. Kakimoto, J. Ozaki and S. Miyata, *J. Phys. Chem. C*, 113 (2009) 20148
 24. Y. Tang, B. Allen, D. R. Kauffman, A. Star, *J. Am. Chem. Soc.*, 131 (2009) 13200
 25. Z. Chen, D. Higgins, H. Tao, R. S. Hsu and Z. Chen, *J. Phys. Chem. C*, 113 (2009) 21008
 26. Z. Chen, D. Higgins and Z. W. Chen, *Carbon*, 48 (2010) 3057
 27. W. Xiong, F. Du, Y. Liu, A. Peres, M. Supp, T. S. Ramakrishnan, L. Dai and L. Jiang, *J. Am. Chem. Soc.*, 132 (2010) 3057
 28. D. Yu, Q. Zhang and L. Dai, *J. Am. Chem. Soc.*, 132 (2010) 15127
 29. Z. Yang, Z. Yao, G. Li, G. Fang, H. Nie, Z. Liu, X. Zhou, X. Chen and S. Huang, *ACS Nano*, 6 (2012) 205
 30. S. Wang, D. Yu and L. Dai, *J. Am. Chem. Soc.*, 133 (2011) 5182
 31. R. Kerr, C. Pozo-Gonzalo, M. Forsyth, and B. Winther-Jensen, *ECS Electrochem. Lett.*, 2 (2013) F29
 32. J. Ma, X. Wang and X. Jiao, *Int. J. Electrochem. Sci.*, 7 (2012) 1556
 33. L. Pigani, A. Heras, Á. Colina, R. Seeber and J. López-Palacios, *Electrochem. Commun.*, 6 (2004) 1192
 34. A. J. Bard, L. R. Faulkner, *Electrochemical methods: fundamentals and applications*, 2nd ed., *John Wiley & Sons, Inc., Hoboken, NJ*, 2001.
 35. S. Wang, D. Yu and L. Dai, *J. Am. Chem. Soc.*, 133 (2011) 5182
 36. S. Patra, N. Munichandraiah, *Langmuir*, 25 (2009) 1732