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ARTICLE

A Facile One-step Synthesis of Co_9S_8 Electrocatalyst for Oxygen Reduction Reaction

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Abstract: A Co-based chalcogenide electrocatalyst has been synthesized by a facile one-step reaction of dodecacarbonyltetracobalt [$Co_4(CO)_{12}$] and elemental sulfur in 1, 6-hexanediol solvent under refluxing conditions. The characterizations of the synthesized compound were performed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD shows the formation of cubic structure Co_9S_8 and SEM micrograph displays cauliflower-like surface morphologies. The catalyst has an open circuit potential (OCP) of 0.75 V (vs. NHE) and shows a promising catalytic activity for the oxygen reduction. The transfer coefficient and Tafel slope are calculated to be 0.50 and 119 mV in the potential region limited by charge transfer kinetics, respectively. The catalytic activity and the electrochemical stability of the catalyst have also been compared with a commercial Pt catalyst.

Key words: oxygen reduction; non-noble metal catalyst; cobalt sulfide; polymer electrolyte membrane fuel cells

Polymer electrolyte membrane fuel cell (PEMFC) has been becoming an interesting electrochemical device for its principal applications in the areas of transportation, stationary power, portable electronic devices in recent years[1,2]. The conventional catalyst for oxygen reduction reaction (ORR) in PEMFC is platinum and platinum-based materials with favorable catalytic activity and chemical stability in acidic medium[3-5]. However, large-scale production and commercialization of the fuel cell are restricted by high cost and scarce resource of the noble metal[6-8]. Despite platinum-based materials possess the best catalytic properties towards the ORR, the sluggish oxygen reduction kinetics and expensive price must be considered. Therefore, it is a significant technological goal to research new inexpensive electrocatalysts to replace platinum. In order to decrease the cost of PEMFC cathode catalysts, several platinum-free catalyst systems such as transition metal chalcogenides [9-12], transition metal macrocyclic compounds[13] and carbon materials[14,15] have been widely studied for decades.

In non-platinum electrocatalysts towards the ORR, transition metal chalcogenides have attracted great attention since Alonso-Vante et al.[16] published Ru-based chalcogenide catalysts having high catalytic activity and stability in acidic electrolyte. In recent years, non-noble transition metal chalcogenide catalysts such as Co-based compounds[17,18] have been considered as a promising alternative due to their low price and availability. The catalytic activity of the Co-based sulfides such as Co_3S_4 and Co_9S_8 for ORR in acid electrolytes was first investigated by Baresel and Behret et al.[19,20]. They found that Co_9S_8 compound had the highest catalytic activity for oxygen reduction among several Co-based sulfides. The catalytic activity of Co_9S_8 catalyst was also predicted by the slab band quantum computational approach [21]. At present, Co_9S_8 compound is mainly obtained by a solid state reaction method [22,23] and the decomposition of the diethyldithiocar-bamate cobalt complexes or the direct conversion of sulfate cobalt in a controlled H_2/H_2S atmosphere[24,25]. The compound could be also prepared by low temperature hydrothermal/solvothermal method [26-28]. However, no correlative studies have been reported concerning Co_9S_8 compound prepared by the reaction of cobalt carbonyl with elemental sulfur in 1, 6-hexanediol

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solvent under the refluxing condition.

In this study, we aimed to synthesize Co_9S_8 compound through the pyrolysis of dodecacarbonyltetracobalt $[Co_4(CO)_{12}]$ and elemental sulfur as precursors in 1, 6-hexanediol solvent under refluxing conditions, an environmentally friendly method prepared the Co_9S_8 catalyst. The obtained catalyst was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The kinetics and activity of the catalyst for the ORR were evaluated by the rotating disk electrode (RDE) technique in 0.5 mol/L H_2SO_4 electrolyte at 25 °C. The synthesized catalyst displayed a promising catalytic activity for oxygen reduction reaction, and had an OCP value of 0.75 V (vs. NHE). The average electron transfer number during the reduction per oxygen molecule was determined to be 3.5 for the catalyst.

1 Experiment

1.1 Catalyst synthesis

The Co_9S_8 catalyst was synthesized by a low temperature refluxing method, as previously reported[29]. Briefly, 0.102 mmol $Co_4(CO)_{12}$ and 0.814 mmol elemental sulfur reacted in a chemical reactor containing 150 mL of 1, 6-hexanediol solvent under refluxing conditions for 5 h. Then, the system was cooled to room temperature, and added 50 mL ultra-pure water and 30 mL ethyl acetate were added. The precipitated powder was recovered from the reaction medium with centrifugation. The black powder was washed ultrasonically with ethylic ether, to eliminate the un-reacted precursor and the organic reaction medium. The resulting catalyst was dried overnight at room temperature.

1.2 Physical characterization

The phase structure of the synthesized catalyst was analyzed by X-ray diffractometer (XRD, Rigaku Corporation D/max-rB) operated at 40 mA and 45 kV using Cu Kα radiation (0.154 18 nm). The XRD pattern was recorded between 10 ° and 70 ° with a scanning rate of 5 ° per minute. The phase structure was identified using the JCPDS data base. A scanning electronic microscope (SEM, FEI Quanta 200) was employed for obtaining SEM images. The surface morphology was carried out at 15.0 kV working voltage.

1.3 Electrode preparation and electrochemical measurements

The electrochemical experiments were performed in a single three-electrode test cell using an electrochemical workstation (Model CHI 660 C, Shanghai Chenhua Instrument Co., Ltd.) at 25 °C. All potentials were expressed against the normal hydrogen electrode (NHE). The 0.5 mol/L H_2SO_4 electrolyte used in these experiments was prepared with 95% sulfuric acid and ultra-pure water. Platinum wire and mercury sulfate electrode (Hg/Hg_2SO_4/0.5 mol/L H_2SO_4) were used as the counter and the reference electrodes, respectively. The working electrode was a polished glassy carbon (GC) disk with geometric area of 0.1256 cm^2. Ink-type catalyst was prepared by dispersing 4 mg catalyst powder in 1 mL ultra-pure water and the resulting mixture was sonicated for 15 min. A 8 μL drop of catalyst ink was deposited onto the glassy carbon surface and the water was evaporated in air. After drying, the powder was covered using a thin Nafion film by adding 6.5 μL of a mixture of ethanol containing 5 wt% Nafion. Then, the coated electrode was dried at room temperature. The estimated amount of catalyst on the working electrode surface was about 255 $\mu g/cm^2$. For comparison, a commercial Pt catalyst working electrode was prepared by the same way.

The rotating disk electrode (RDE) voltammetric measurements were accomplished using variable speed rotator (Model ATA-1B, Jiangsu Jiangfen Electroanalytical Instrument Co., Ltd.). Before the electrochemical measurements, the working electrode was activated by potential cycling between 0.80 and 0.05 V (vs. NHE) for 20 min at a scan rate of 25 mV/s in 0.5 mol/L H_2SO_4 solution outgassed with purified nitrogen. Then, the electrolyte was saturated with pure oxygen for 30 min and maintained oxygen atmosphere above the solution surface during the electrochemical measurements. The linear sweep voltammetry (LSV) test was carried out at a scan rate of 10 mV/s. The rotation speed of the working electrode ranged from 100 to 2500 r/min. The electrochemical stability and catalytic activity of the catalyst was measured by chronoamperometry at fixed potential of -0.2V.

2 Results and Discussion

2.1 Catalyst characterization

Fig. 1 shows XRD pattern of the as-synthesized Co-S catalyst and vertical bars representative ICDD-PDF-1998 card of Co_9S_8 No. 75-2023. The similarity in diffraction peak positions between the sample and the card demonstrates that a successful synthesis of Co_9S_8 with cubic structure was accomplished. The structure of the Co_9S_8 catalyst is consistent with the results reported in the literature[23]. No obvious impurity phases were detected by XRD, indicating that the prepared Co_9S_8 powder presents a good state of purity. The average crystallite size of the powder was calculated according the Scherrer equation[30]:

$$D_{hkl} = K\lambda/(\beta\cos\theta) \quad (1)$$

where, K is a constant (0.89), λ is the X-ray wavelength (0.154 18 nm), β is the measured full-width at half-maximum (FWHM) and θ is the reflection angle. The average particle size of 22.3±0.5 nm was obtained based on (311), (222) and (440) diffraction plane.

Fig. 2 shows SEM image of the as-synthesized Co_9S_8 compound. It can be observed that the catalyst particles are crude in nature, and there is a substantial agglomeration of the particles. The particle aggregates with the order of 115~170 nm in size are evenly distributed, but some larger

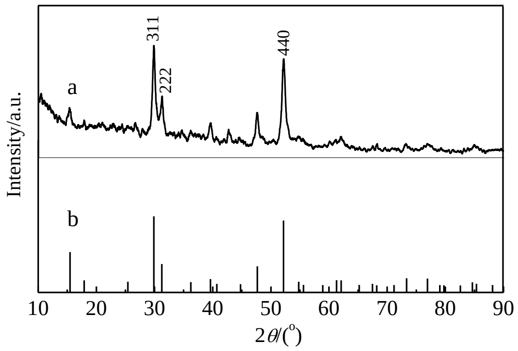

Fig. 1 XRD patterns of as-synthesized Co_9S_8 catalyst (a) and representative ICDD-PDF-1998 cards of Co_9S_8 No. 75-2023 (b)

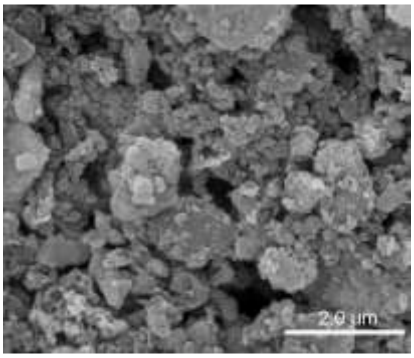

Fig. 2 SEM micrograph of the as-synthesized Co_9S_8 catalyst

particles (0.5~1.5 μm) are also observed in the sample. The catalyst powder exhibits similar cauliflower surface morphology, which can be an advantageous property for the electrochemical oxygen reduction[31].

2.2 Electrocatalytic properties analysis

In order to evaluate the catalytic activity of the synthesized catalyst towards the ORR, linear sweep voltammetry (LSV) tests were carried out. Fig.3 shows polarization curves of electrochemical reduction of molecular oxygen on the Co_9S_8 catalyst in 0.5 mol/L H_2SO_4 obtained using RDE at a scan rate 10 mV/s. The larger cathodic current density was obtained in the oxygen saturated electrolyte compared to those in nitrogen, and the current density for the ORR might be attribute to the high crystallization of the compound[32]. The current density of ca. 0.26 mA/cm^2 at 0.5 V (vs. NHE) at 1600 r/min is higher than current density of 0.10 mA/cm^2 for Co_9S_8 microspheres prepared by solvothermal method[29]. However, the value is lower than that of $Co_{1-x}S$-graphene hybrid[33] and $CoSe_2$/C nanoparticles[34], indicating that the catalytic activity of the Co_9S_8 compound must be further improved. The cathodic current density depended markedly on rotation rate of the RDE, and the current density would be enhanced by increasing the rotation rate at lower potential region. A charge transfer kinetic control for oxygen reduction is observed above 0.62 V (vs. NHE), because the current density does not depend on rotation rate in the potential range. The ORR is controlled by the mixed kinetic-diffusion process at more cathodic potential than 0.62 V (vs. NHE). However, the acclivitous current plateau was recorded as shown in Fig. 3, indicating that the distribution of the electrocatalytic active sites on the electrode surfaces is less uniform and the catalytic reaction is slower[35]. The OCP value of 0.75 V (vs. NHE) in the oxygen saturated electrolyte is comparable to the predicted value 0.74 V (vs. NHE) for Co_9S_8[22]. However, this value is lower than that of Co_3S_4 (0.80 V, vs. NHE) synthesized by high temperature[20].

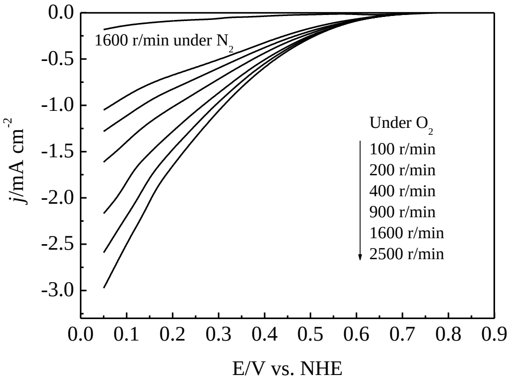

Fig. 3 Polarization curves of oxygen reduction on Co_9S_8 catalyst in 0.5 mol/L H_2SO_4 saturated with oxygen at different rotation speed. The currents were recorded at a scan rate of 10 mV/s

In the RDE surface, the overall measured current density (j) is related to the kinetic current density (j_k) and the diffusion current density (j_d) by the Koutecky-Levich equation[36]:

$$\frac{1}{j}=\frac{1}{j_\mathrm{k}}+\frac{1}{j_\mathrm{d}}=\frac{1}{j_\mathrm{k}}+\frac{1}{B\omega^{1/2}} \tag{2}$$

where, ω is the rotation rate per minute, B is the Levich slope, given by:

$$B=0.2nFC_\mathrm{O}D_\mathrm{O}^{2/3}v^{-1/6} \tag{3}$$

where, D_O is the oxygen diffusion coefficient, C_O is the oxygen solubility v is the kinematic viscosity, n is the number of electron transferred per molecule of O_2 reduced, and F is the Faraday constant.

Fig. 4 shows the Koutecky-Levich plots for the Co_9S_8 catalyst from the data of Fig. 3. The plots of *1/j* vs $\omega^{-1/2}$ for potential range of 0.20~0.35 V (vs. NHE) yield a series of essentially parallel straight lines having a slope value of *B*. The average value of *B* is 8.35×10^{-2} mA·cm^{-2}·r$^{-1/2}$·min$^{1/2}$, while the theoretical value calculated for the four-electron

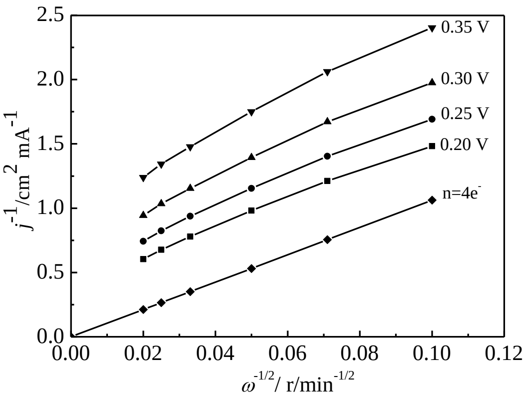

Fig.4 Koutecky-Levich plots for O_2 reduction on the Co_9S_8 catalyst at various potentials obtained from the data of Fig. 3

transfer in the ORR is 9.41×10^{-2} mA cm^{-2} r$^{-1/2}$ min$^{1/2}$ [37]. The calculated number of electrons transferred during an oxygen molecule reduction from the slop is 3.5, indicating that the ORR on the catalyst could follow a four-electron reduction mechanism. For Co_9S_8 compound, S^{2-} could provide an adsorption site for O atom promoting oxygen reduction process[21]. The linearity and parallelism of the all lines in Fig. 4 indicates that the electron number transferred per oxygen molecule and the active surface area of the catalyst towards the ORR does not obviously change in the potential range measured[35].

Fig. 5 shows the polarization curves of the ORR on the Co_9S_8 catalyst in O_2-saturated 0 and 1.0 mol/L methanol containing 0.5 mol/L H_2SO_4 solution at RDE rotating speed of 1600 r/min at 25 °C. It is obvious that the current density of oxygen reduction is less influenced by methanol, suggesting that the catalyst shows good methanol tolerance and high selectivity to ORR.

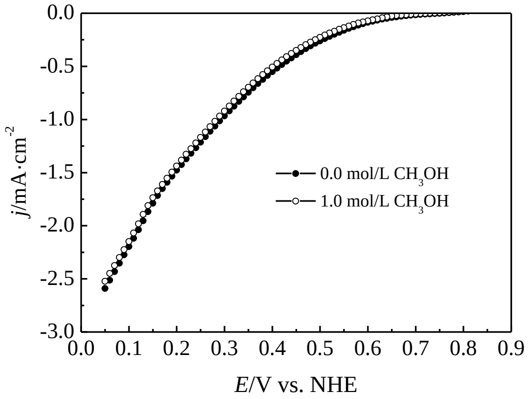

Fig. 5 Steady-state polarization curves for the ORR on the Co_9S_8 catalyst in O_2-saturated 0 and 1.0 mol/L methanol containing 0.5 mol/L H_2SO_4 solution at 25 °C, respectively (the electrode rotating speed was 1600 r/min, and the currents were recorded at a sweep rate of 10 mV/s)

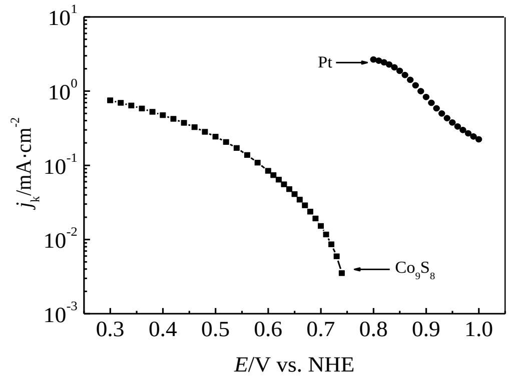

Fig.6 Mass transfer corrected Tafel plots for oxygen reduction on Co_9S_8 and Pt catalyst in 0.5 mol/L H_2SO_4 saturated with oxygen at 25 °C

Fig. 6 shows the mass transfer corrected Tafel plots of the Co_9S_8 and a commercial Pt (J. M. Company) catalyst obtained from a RDE polarization curves in 0.5 mol/L H_2SO_4 solution saturated with oxygen. It is obvious that the kinetic current density of the Co_9S_8 catalyst for the oxygen reduction is lower than that of the commercial Pt catalyst. The Tafel slope, exchange current density and transfer coefficient of the synthesized Co_9S_8 catalyst obtained in the analyzed potential range are −119 mV, 5.14×10^{-7} mA/cm² and 0.50, respectively. The Tafel slope and the transfer coefficient are closer to the theoretical values, indicating that the ORR on the Co_9S_8 catalyst is controlled by the first electron transfer process in the measured potential range[38,39]. The exchange current density (j_o) on the Co_9S_8 catalyst is much lower than that of the commercial Pt catalyst (1.54×10^{-3} mA/cm²) under the same conditions, indicating that the kinetic property of the synthesized catalyst must be further improved.

2.3 Evaluation of electrochemical stability

To investigate the electrochemical stability of the catalyst in the acid solution during oxygen reduction, chronoamperometry was carried out during 1000 s at fixed potential of −0.2 V, as shown in Fig. 7. The data of a commercial platinum catalyst are also included for comparison. It is also clear that the Co_9S_8 catalyst shows a lower current density towards oxygen reduction and higher decay rate of catalytic activity, compared with the commercial platinum catalyst. The results suggest that the electrochemical stability and catalytic activity of the Co_9S_8 catalyst should be further improved.

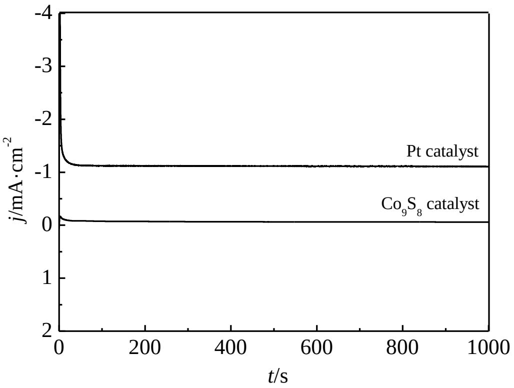

Fig.7 Results from chronoamperometry for Co_9S_8 and Pt catalyst in O_2-saturated 0.5 mol/L H_2SO_4 solution at −0.2V

3 Conclusions

1) Co_9S_8 nanoparticles are synthesized by a facile one-step method in 1, 6-hexanediol solvent under refluxing conditions. The synthesized catalyst shows cubic crystalline structure Co_9S_8 and cauliflower-like surface morphologies.

2) The OCP value of 0.75 V (vs. NHE) in the oxygen saturated 0.5 mol/L H_2SO_4 electrolyte is comparable to the predicted value 0.74 V (vs. NHE) for Co_9S_8. The electron transferred process of 3.5 is determined during the reduction per oxygen molecule under the experimental conditions. A Tafel slope of −119 mV and a transfer coefficient of 0.50 for the catalyst are obtained in the kinetic control region.

3) The stability of the sample to be used as electrocatalyst for oxygen reduction in H_2SO_4 solution should be further enhanced.

References

1 Hyun K, Lee J H, Yoon C W *et al. International Journal of Electrochemical Science*[J], 2013(8): 11 752
2 Ozdemir O K. *Electrochemistry*[J], 2015, 83: 76
3 Gasteiger H A, Kocha S S, Sompalli B *et al. Applied Catalysis B*[J], 2005, 56: 9
4 Shao Y Y, Zhang S, Wang C M *et al. Journal of Power Sources*[J], 2010, 195: 4600
5 Cheng N, Banis M N, Liu J *et al. Advanced Materials*[J], 2015, 27: 277
6 Wang S, Yu D, Dai L. *Journal of the American Chemical Society*[J], 2011, 133: 5182
7 Wang J J, Chen Y G, Liu H *et al. Electrochemistry Communications*[J], 2010, 12: 219
8 Zhang S, Shao Y, Liao H *et al. Chemistry of Materials*[J], 2011, 23: 1079
9 Feng Y, Gago A S, Timperman L *et al. Electrochimica Acta*[J], 2011, 56: 1009
10 Duan D, Liu S, Niu X *et al. Rare Metal Materials and Engineering*[J], 2011, 40(7): 1282 (in Chinese)
11 Zhao D J, Ma S Y. *Rare Metal Materials and Engineering*[J], 2014, 43(4): 846 (in Chinese)
12 Zhao D J, Ma S Y. *Chemical Research in Chinese Universities*[J], 2015, 31: 447
13 Kothandaraman R, Nallathambi V, Artyushkova K *et al. Applied Catalysis B*: *Environmental*[J], 2009, 92: 209
14 Yang Z, Nie H, Chen X *et al. Journal of Power Sources*[J], 2013, 236: 238
15 Zhai H, Cao L, Xia X. *Chinese Chemical Letters*[J], 2013, 24: 103
16 Alonso-Vante N, Tributsch H. *Nature*[J], 1986, 323: 431
17 Gao M, Jiang J, Yu S. *Small*[J], 2012, 8: 13
18 Li H, Gao D, Cheng X. *Electrochimica Acta*[J], 2014, 138: 232
19 Baresel V D, Sarholz W, Scharner P *et al. Berichte Der Bunsengesellschaft Für Physikalische Chemie*[J], 1974, 78: 608
20 Behret H, Binder H, Sandstede G. *Electrochimica Acta*[J], 1975, 20: 111
21 Sidik R A, Anderson A B. *Journal of Physical Chemistry B*[J], 2006, 110: 936
22 Morris B, Johnson J, Wold A. *Journal of Physics and Chemistry of Solids*[J], 1967, 28: 1565
23 Schneemeyer L F, Sienko M J. *Inorganic Chemistry*[J], 1980, 19: 789
24 Cui H, Pike R D, Kershaw R *et al. Journal of Solid State Chemistry*[J], 1992, 101: 115
25 Zhan J H, Yang X G, Xie Y *et al. Journal of Materials Research*[J], 1999, 14: 4418
26 Qian X F, Zhang X M, Wang C *et al. Inorganic Chemistry*[J], 1999, 38: 2621
27 Wang C, Zhang X M, Qian X F *et al. Journal of Physics and Chemistry of Solids*[J], 1999, 60: 2005
28 Zhou Y X, Yao H B, Wang Y *et al. Chemistry-A European Journal*[J], 2010, 16: 12 000
29 Zhao D, Zhang S, Yin G *et al. Journal of Power Sources*[J], 2012, 206: 103
30 Patterson A L. *Physical Review*[J], 1939, 56: 978
31 Borja-Arco E, Castellanos R H, Uribe-Godinez J *et al. Journal of Power Sources*[J], 2009, 188: 387
32 Vayner E, Sidik R A, Anderson A B. *Journal of Physical Chemistry C*[J], 2007, 111: 105 08
33 Wang H, Liang Y, Li Y *et al. Angewandte Chemie-International Edition*[J], 2011, 50: 10 969
34 Feng Y J, He T, Alonso-Vante N. *Fuel Cells*[J], 2010, 10: 77
35 Suarez-Alcantara K, Rodriguez-Castellanos A, Dante R *et al. Journal of Power Sources*[J], 2006, 157: 114
36 Zhang S, Shao Y Y, Yin G P *et al. Journal of Materials Chemistry*[J], 2010, 20: 2826

37 Hsueh K L, Chin D T, Srinivasan S. *Journal of Electroanalytical Chemistry*[J], 1983, 153: 79

38 Clouser S J, Huang J C, Yeager E. *Journal of Applied Electrochemistry*[J], 1993, 23: 597

39 Alonso-Vante N, Tributsch H, Solorza-Feria O. *Electrochimica Acta*[J], 1995, 40: 567

简单一步法合成 Co_9S_8 氧还原反应电催化剂

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摘　要：采用低温回流技术，以$Co_4(CO)_{12}$和S粉为原料，在1, 6-己二醇溶剂中一步合成了钴硫化物催化剂。用X射线衍射仪和扫描电子显微镜对合成的化合物进行了表征。XRD分析表明合成样品为立方结构的Co_9S_8化合物，其SEM图片显示了花椰菜状的表面形貌。Co_9S_8化合物表现出良好的氧还原催化活性，开路电位为0.75 V（vs. NHE）。在电荷转移控制电位区，电极反应传递系数和塔菲尔斜率分别为0.50和119 mV。同时，将催化剂的催化活性和电化学稳定性与商业铂催化剂进行了比较。

关键词：氧还原；非贵金属催化剂；钴硫化物；聚合物电解质膜燃料电池

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