Iranian Journal of Hydrogen & Fuel Cell 3(2017) 231-240

Iranian Journal of Hydrogen & Fuel Cell

IJHFC

Journal homepage://ijhfc.irost.ir

Facile synthesis of N, S-doped graphene from sulfur trioxide pyridine precursor for the oxygen reduction reaction

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Article Information

Article History:

Received:
26 Dec 2017
Received in revised form:
22 Jan 2018
Accepted:
27 Jan 2018

Keywords

Co-doped graphene
Metal-free catalyst
Oxygen reduction reaction

Abstract

In the work presented here, nitrogen and sulfur co doped on porous graphene was synthesized using pyrolysis at 900°C for 2h and the hydrothermal technique at 180°C for 24 h as metal-free electrocatalysts for oxygen reduction reaction (ORR) under alkaline conditions. All the materials have been characterized by Scanning Electron Microscopy (SEM) and X-ray photo-electron spectroscopy (XPS). Moreover for electrochemical evaluation of samples, the Rotating Disk electrode (RDE) and Cyclic Voltammetry techniques (CV) were employed. The results showed that co-doping of S and N into porous graphene significantly enhance the ORR performance. Moreover, it is revealed that the catalyst prepared by the pyrolysis method shows outstanding catalytic activity for the ORR for which the number of electron in the pyrolysis method was calculated to be 4.1; whereas, it became 2.6 in the hydrothermal approach.

So regarding the obtained results, it can be stated that the samples prepared through the pyrolysis method exhibits excellent resistance towards methanol crossover effects, indicating their promising potential as ORR electrocatalysts for alkaline fuel cells.

1. Introduction

One of the most important devices for clean energy production is fuel cells, in which electrocatalysts have an important role in the Oxygen reduction reaction (ORR).

Extensive researches have been made to synthesise new high efficient metal free electrocatalysts [1, 2]

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doi: 10.22104/ijhfc.2018.2685.1162

because of their low cost and poisoning effects, high stability, crossover and durability [2-4].

Due to their electrical conductivity and activity hetero-atom doped carbon materials, such as N, S, B, P doped carbon, have been recently applied in electrocatalysis ORR, supercapacitors, and metal-air batteries [5]. Graphene, a single layer of graphite, has many advantages, such as overall chemical inertness, remarkable structure, notable electronic properties, and relative facile preparation, when used as electrocatalyst [6]. Moreover, heteroatom-doped graphene nanosheets not only enhance the electrical properties of graphene, but also effectively create a more active site of the catalyst toward ORR [7-12].

Unfortunately due to the natural aggregation of graphene sheets and low content of doped atoms, the modified doped graphene materials show some ORR performance limitations. Therefore to further improve the ORR efficiency, effective methods of doping graphene with two heteroatoms need to be proposed because of synergistic effects between dopants [13]. Instead of increasing the doping level of a single heteroatom it is possible to codope graphene with two different heteroatoms, which is a promising option for electrochemical applications that will be able to create defect sites as ORR active sites.

Different approaches have been used to introduce hetero-atoms within the graphene framework. Most of these are complex due to working at high temperatures in the gas phase or plasma state, microwave treatment, and arc discharge or are unable to control the doping degree and hetero-atoms functionality [14-16]. Such dual doping with N, B or P has been reported but fewer papers have studied the dual doping of graphene with N and S and their catalytic activity towards ORR [17-20]. Most of these methods involve multi-steps and time-consuming procedures as previously mentioned. For example, Liang et al. reported an interesting approach for the synthesis of dual doped mesoporous graphene using colloidal silica template at a temperature of 900°C [17]. Su et al. synthesized a N and S doped 3-dimensional graphene framework using the hydrothermal method at 180°C for 10 h [18]. Xu et al. synthesized N and S doped few-layered graphene oxide for ORR using chemical vapor deposition [19]. Very recently, Ai et al. synthesized N and S doped graphene for catalytic and battery applications; the doping of heteroatom onto the carbon network and reduction of graphene was achieved in two different steps over 36 h [20].

For more comparison, the electrochemical properties of other published heteroatom doped electrocatalyst have been included in Table 1.

So, herein, we compare two facile new approaches for preparation of N, S-doped graphene synthesized by the pyrolysis and hydrothermal technique from sulfur trioxide pyridine as a precursor. The prepared electrocatalyst exhibited good electrocatalytic activity. Furthermore, the studied electrode showed superior stability compared to commercial Pt/C catalysts under alkaline conditions. Of course, the best results were obtained for the sample prepared via the pyrolysis method in comparison to the hydrothermal approach.

2.Materials and synthesis method

Porous graphene (G) was synthesized using the CVD (Chemical vapor deposition) method over the catalyst according to the RIPI (Research Institute of Petroleum and Industry) procedure [5]. Sulfur trioxide pyridine complex, KOH, HCl (37%), Ethanol (99.8%) and Nafion (5 wt. % in lower aliphatic alcohols and water) were purchased from the Sigma-Aldrich Company. Pt/C (20 wt%, Pt on Vulcan XC72) was also obtained from the Sigma-Aldrich Company

To prepare N and S co-doped graphene in the pryrolysis procedure, 100 mg G was dispersed in 100mL ethanol by sonication for 30 min. in an ultrasonic bath. Afterwards, 0.2 g Sulfur trioxide pyridine complex solution was added into the G solution while stirring. The reaction was carried out for 5 h at room temperature and then dried at 60°C. Dried powder was grounded for homogeneity. Then the powder was heat treated at 900 °C for 2 h in a N_2 atmosphere. The catalysts prepared in this manner

Table 1. Comparison of ORR activity between nitrogen, sulfur doped and (N, S) co-doped carbon nanostructures

Synthesis method and precursor	Electrocatalyst	Number of transfers electron (n)	Onset Potential (V vs RHE) *	Reference
Template method/Polyaniline (PANI)	N-O doped mesoporous carbon	4	0.7-0.8	21
Sputtering and annealing	N-doped carbon film	4	0.61-0.76	22
Pyrolysis/sugar+urea	N-doped graphene	4	0.66-0.81	23
Carbonization/nucleobases + ionic liquid	N-doped mesoporous carbon	4.1	0.86-0.91	24
Thermal treatment/glucose + urea	N-doped graphene	3.2-3.7	0.56-0.76	25
Thermal treatment/GO + melamine	N-doped graphene	3.4-3.6	0.76	26
Spray pyrolysis/xylene + ethylenediamine	N-doped carbon spheres	3.86	0.66-0.76	27
Electrochemical approach/ graphene sheets	N-doped graphene quantum dot	3.6-4.4	0.71	28
Template method/3-MBP-dca or CMIM-Cl	N-doped hollow carbon hemisphere	3.82	0.61-0.76	29
CVD (C source, methane; N source, ammonia, Cu)	N-doped graphene	3.6-4	0.71	7
A hard-templating approach	N-doped graphene	3.9	0.7-0.85	30
Hydrothermal reaction/GO + NH4SCN	S, N- co-doped graphene	3.9	0.76	18
CVD/ pyrimidine and thiophene	S, N- co-doped Few-Layered Graphene Oxide	3.7	0.81	13
Comparative study of various types of metal-free N and S co-doped porous graphene for high performance Oxygen reduction reaction in alkaline solution	N,S and N doped nanoporous graphene	4	0.93 for N,S doped 0.91for N doped	21

* All of the electrochemical investigations were conducted in 0.1 M KOH as the electrolyte.

will be here referred to as GSP 900.

Additionally, N-S doped graphene was hydrothermally synthesized from the mixture of porous graphene and sulfur trioxide pyridine complex as the nitrogen and sulfur precursor. 100 mg of G was dispersed in 100 ml deionized water using a cleaner ultrasonic bath. Then, 300 mg of sulfur trioxide pyridine complex was slowly added to the G suspension and stirred for 1hr. Following, the mixture was poured into a Teflon container and put in an oven at 180°C for 24 hr. The catalysts prepared in this manner will be here referred to as GSP h180.

3. Characterization method

The samples morphology was determined using a field emission scanning electron microscope (Mira-TSCAN) and EDS (Energy Dispersive Spectroscopy) mapping with an accelerating voltage of 5.0 kV. The surface chemical composition identification and bonding state were investigated using an X-ray photoelectron spectroscopy (XPS), in which photoelectrons were collected on a Physical Electronics Model 5700 XPS instrument.

4. Electrochemical evaluation

The electrochemical measurements were carried out in a conventional three-electrode cell on the Autolab potentiostat/galvanostat PGSTAT30 electrochemical workstation.

A platinum electrode and Ag/AgCl saturated with KCl were used as the counter and reference electrodes, respectively. Meanwhile, all the calculation has been done based on RHE (Reversible Hydrogen Electrode) according to the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + E^0_{Ag/AgCl} \quad (1)$$

Where E_{RHE} is the converted potential vs. RHE, $E^0_{Ag/AgCl} = 0.1976$ at 25 °C, and $E_{Ag/AgCl}$ is the experimentally measured potential against an Ag/AgCl reference.

The electrocatalytic activity towards ORR was measured in an O_2-saturated 0.1 M KOH solution using a rotating disk electrode. Then, the electron transfer was calculated using the Koutecky–Levich equation [6].

5. Results and discussion

5.1. Catalyst characterization

The surface morphology of the synthesized nitrogen and sulfur doped graphene material was evaluated by a field emission scanning electron microscope (FESEM) (Fig. 1).

The elemental mapping distribution exhibited good and uniform dispersion of these elements in the carbon structure confirming nitrogen and sulfur have been successfully distributed in the graphene base.

In addition, XPS measurement was used to probe the nitrogen and sulfur atoms in the co-doped porous graphene structure. The High resolution XPS spectra of the N peak in Fig. 2 shows pyridinic (~398.5 eV) and pyrrolic (~400.6 eV) nitrogen species, both of which are important phases for the ORR process. Also, a strong S 2p peak represents a significant amount of S doped atoms, which the deconvolution analysis shows as a peaks around 163.8 (85%), 165.0 (10%) and 168.8 (5%) of the S, 2p are evidence of the presence of C-S, sulfoxide and other oxidized forms.

5.2. Electrochemical Evaluation

The effect of preparation methods in the synthesized electrocatalysts was investigated by the Cyclic Voltammetry (CV) and Rotating Disk electrode

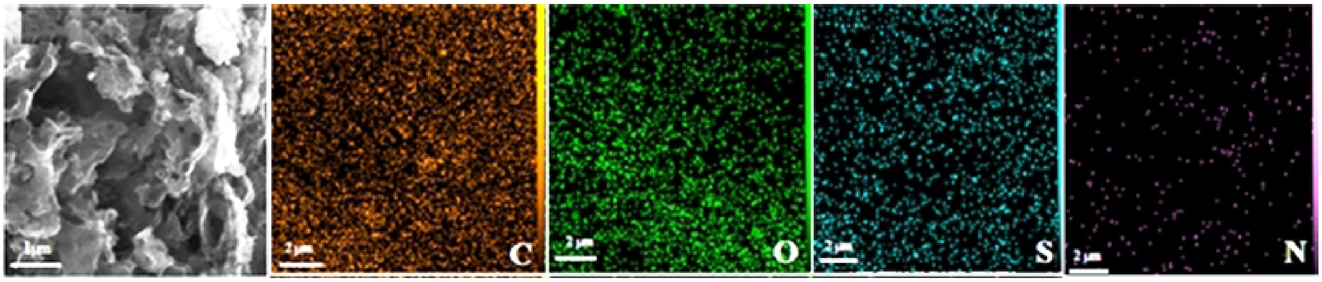

Fig. 1. FESEM micrographs and EDX mapping analysis of GSP 900.

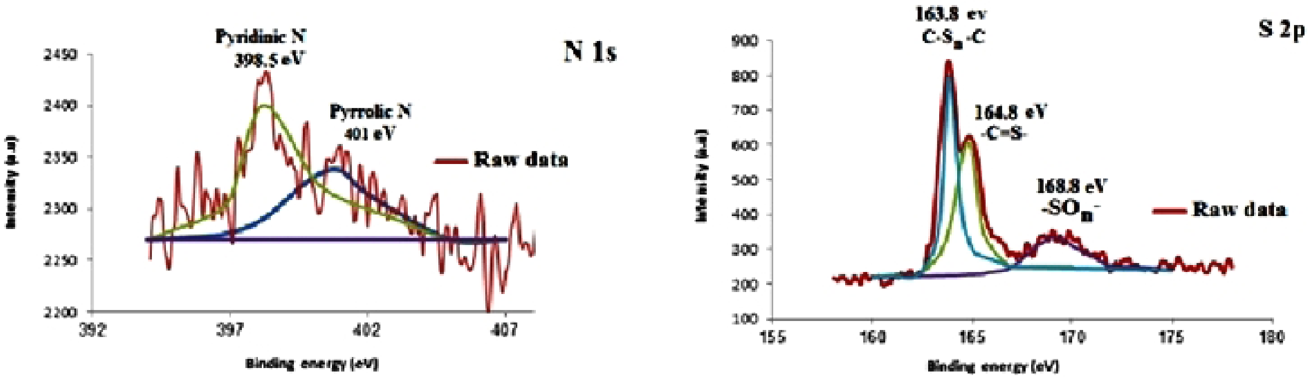

Fig. 2. The XPS high resolution spectra of GSP 900.

(RDE) techniques.

The CV evaluation of the prepared catalysts with different preparation procedures is shown in Fig. 3, and is also compared to G and Pt 20.

All the catalysts showed a more positive onset potential and higher ORR reduction peak than G, and were accompanied with an increase in the peak current density for all the prepared samples. The trend of increased potential is according to: G < GSP h180< GSP 900<Pt/C commercial. These results clearly indicate that the co-doped nitrogen and sulfur to graphene structure could enhance the catalytic activity, and among the co-doped samples, GSP 900 (the sample prepared by the pyrolysis method) shows a higher peak current density and ORR performance than the GSP h180, due to formation of more ORR active sites. This implies that in the sulfur trioxide pyridine complex one S atom is out of the aromatic ring and one N atom in the ring, which makes it decompose at high temperatures and allows decomposition and doping to take place simultaneously [31].

In addition, LSV measurements were performed on the samples. A comparison of the LSV graphs of the prepared samples is shown in Fig. 4. According to this figure, the ORR of the G electrode commenced

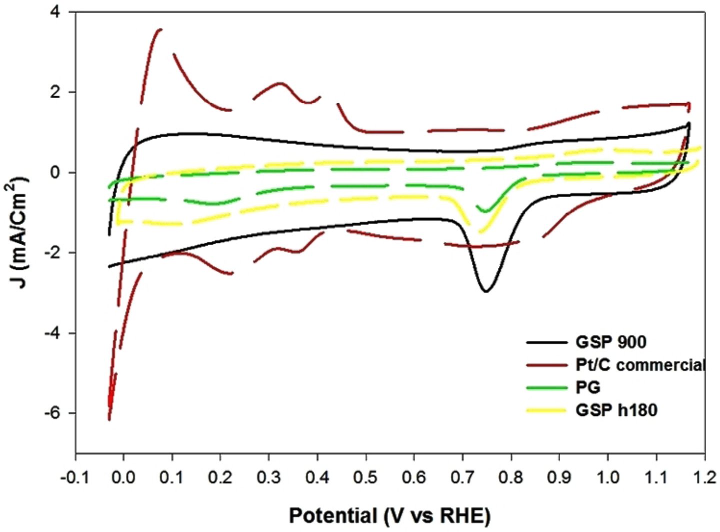

Fig. 3. Cyclic voltammograms of electrocatalysts for alkaline oxygen reduction in O_2 saturated with different methods of preparation.

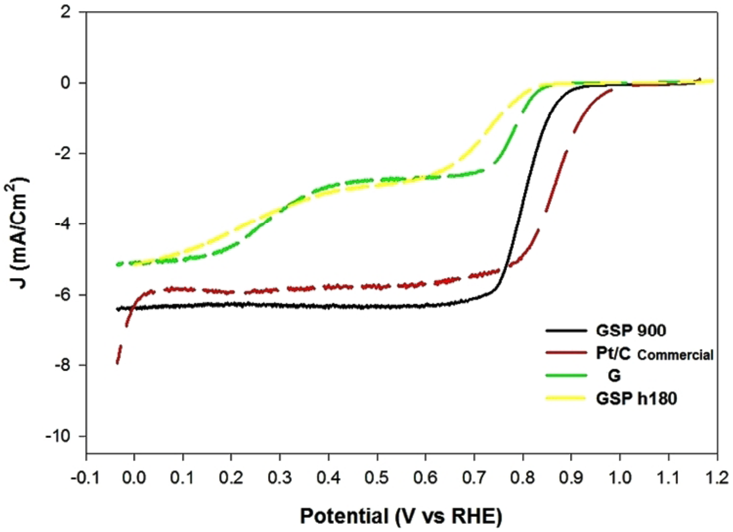

Fig. 4. Comparison of linear sweep voltammetry at 1500 rpm, for the electrocatalysts prepared by different procedures, in O_2 saturated KOH 0.1 M.

at around 0.85 V (onset potential), whereas the ORR onset potential of the GSP 900 electrode was around 0.93 V, which is higher than the porous graphene. This suggests that due to the presence of nitrogen and sulfur in suitable active sites for ORR, it has a more efficient oxygen reduction confirm the other obtained electrochemical results.

Also, the number of electrons transferred (n) per oxygen molecule involved in the ORR process are quantitatively calculated using the Koutechy–Levich equation for Pt/C commercial and GSP 900 samples (Fig. 5). the results showed 4.1 for GSP 900 confirming a 4 e- ORR pathway similar to that of Pt/C commercial, and 2.1 in the case of GSP h180. However, the electrochemical results confirm the better performance and activity of the sample prepared by pyrolysis method.

a mixture of gases. The flows of H_2 and O_2 are in opposite directions. The mass flow rates at the anode and cathode are 5.599375×10^{-7} and 9.843×10^{-6} (kg/s), respectively. The outlet boundary condition is the pressure outlet. The voltages are 0.4, 0.5, 0.6, 0.7, 0.8 and 0.95 (V) were selected for their potential in solving the reaction. The species concentration on the cathode side of H_2, O_2, and H_2O are 0, 0.1785 and 0.15 (mol/m^3), respectively, and on the anode side are 0.5, 0 and 0.5 (mol/m^3), respectively. The CL porosities of anode and cathode are 0.4, 0.5 and 0.6. The GDL porosities are changed as follows: 0.7, 0.82 and 0.92. The no-slip boundary condition is imposed on the walls. Some model parameters are affected by the compression or operating conditions (e.g. GDL porosity and electric conductivity). The briefed values for the parameters are tabulated in Table 2.

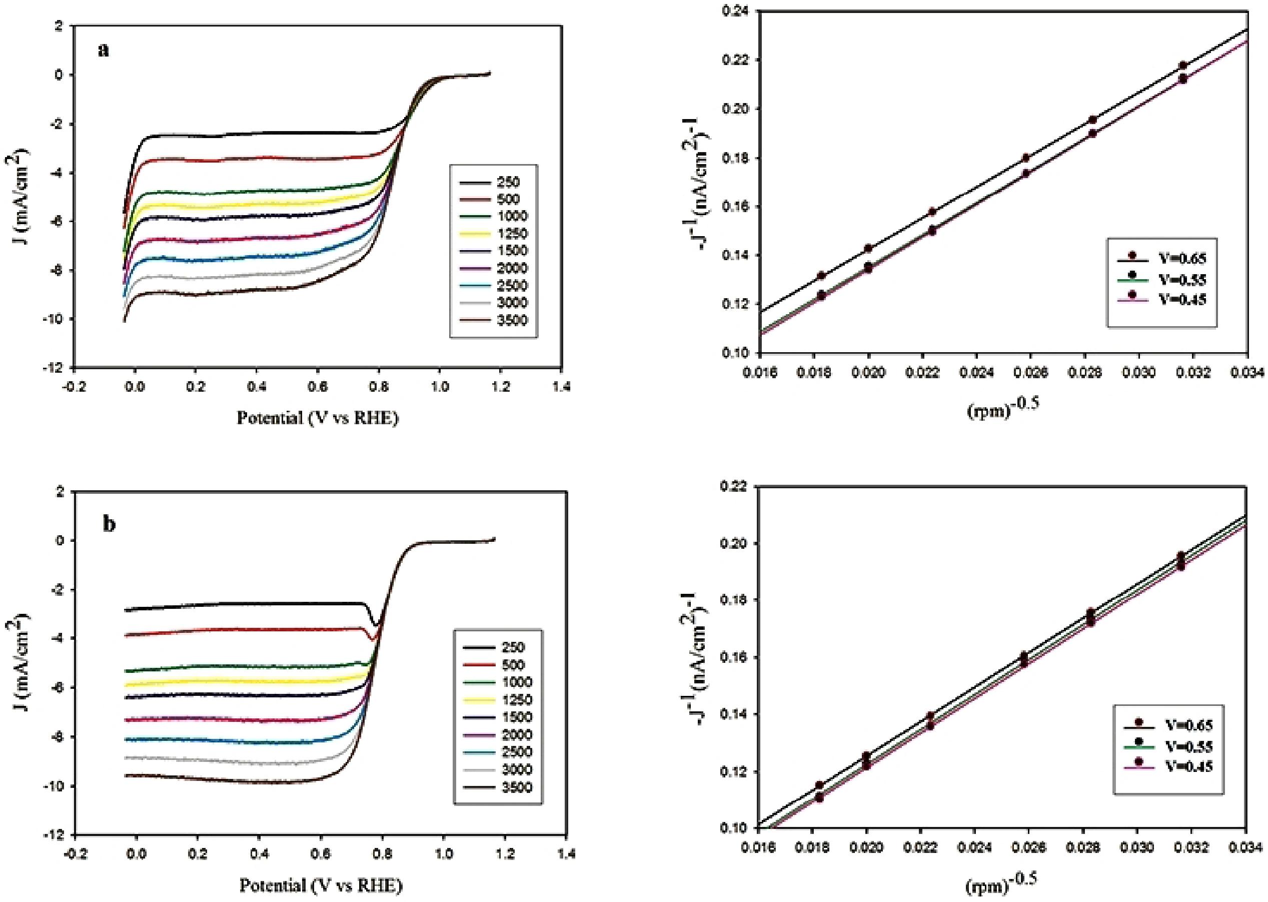

Fig. 5. Linear sweep voltammetry at different rotation rates of a) Pt/C commercial and b) GSP 900,(scan rate 5 mV/sec). The corresponding Koutecky–Levich plots are shown at different potentials.

5.3. Tafel analysis

Also, the tafel plot obtained from LSV data (Fig. 6) gives the kinetic currents [32-33].

As can be seen, the tafel slope in the GSP 900 sample is similar to the Pt/C commercial sample. The over-potential of the doped catalysts is also very close to it.

5.4. Methanol stability test

In addition, the tolerance of the synthesized electrocatalyst sample toward methanol crossover was investigated by adding 1M methanol during the CV measurements.

As can be seen in Fig. 7.a, the oxygen reduction peak of the Pt/C commercial catalyst disappeared after adding methanol. However, a strong and stable CV peak remained at the prepared doped electrode (Fig. 7.b), indicating its excellent tolerance to the crossover effect of methanol.

Therefore, the GSP 900 catalyst exhibits excellent selectivity and durability, showing superior advantages over the commercial Pt/C 20 wt% when used as long-term running electrocatalyst.

Moreover, chronoamperometry analysis is applied to characterize the electrodes stability. The current density-time plots of N, S doped graphene (GSP 900) and Pt/C commercial electrodes in O_2-saturated 0.1 M KOH at the potential of -0.86V for 5000 s are shown in Fig. 8.

The Pt/C commercial sample shows a significant decrease in current density during the time (Fig. 8.a), while the GSP 900 electrocatalyst indicates stable

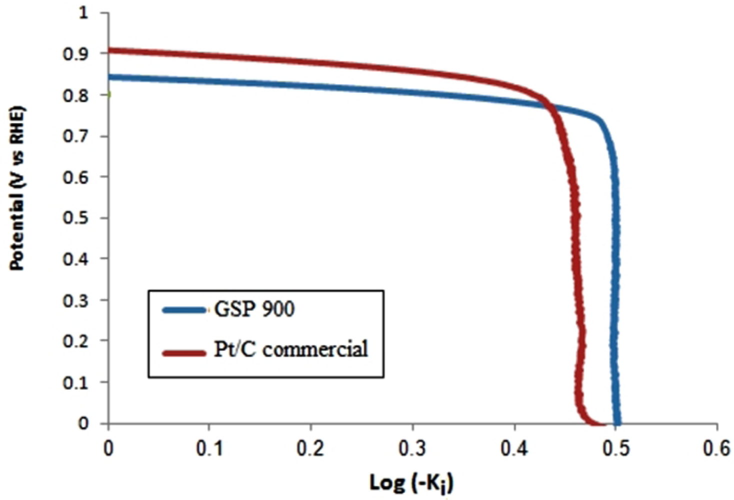

Fig. 6. Tafel plot of the GSP 900 electrocatalyst in comparison to the Pt/C commercial.

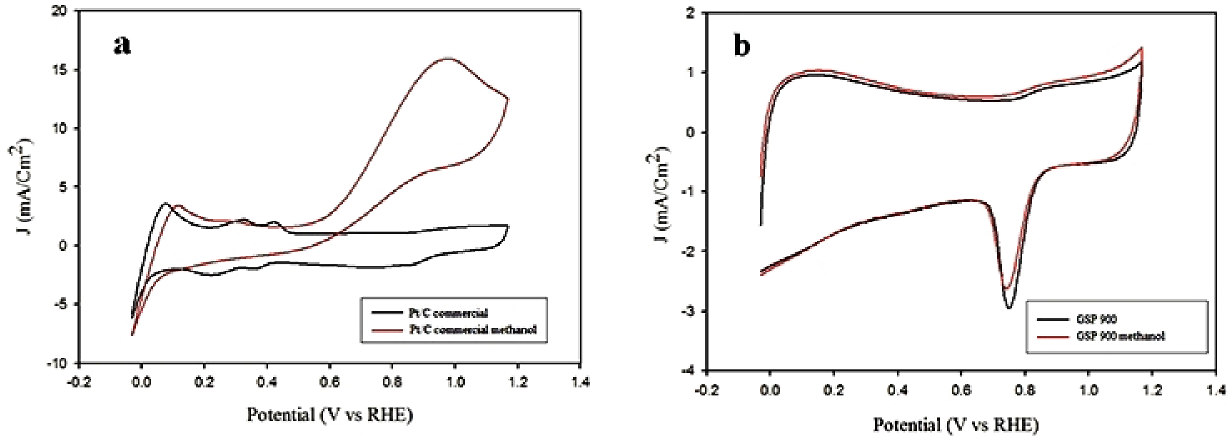

Fig. 7. Cyclic voltammetry of a) Pt/C commercial and b) GSP 900, in KOH 0.1 M (50 mV/sec) before and after adding methanol.

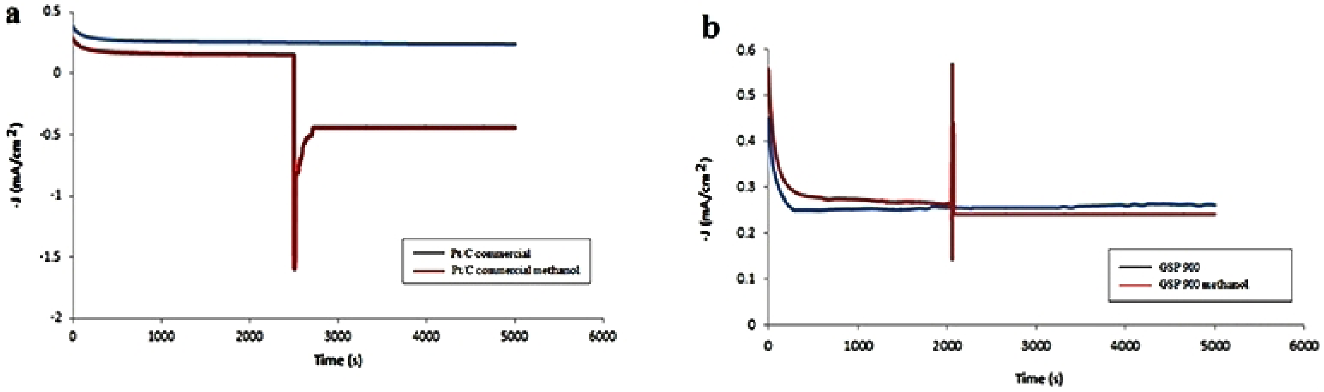

Fig. 8. Current density-time plots for a) Pt/C commercial and b) GSP 900 electrodes in O2 saturated 0.1 M KOH before and after adding methanol.

current density and good methanol tolerance after 5000 s (Fig. 8-b), representing long-term stability for doped graphene catalyst due to the existence of S and N stable phases in the graphene structure.

6. Conclusion

In this work, nitrogen-sulfur co-doped porous graphene electro catalysts were successfully prepared via pyrolysis and hydrothermal methods and their electrochemical performance compared in alkaline ORR. The S, N co-doped graphene catalyst prepared at 900 °C by sulfure trioxide pyridine not only shows the high homogeneity of N and S dispersion in graphene structure, but also has a comparatively ORR performance to Pt 20 wt%. The onset of the catalyst prepared by the pyrolysis procedure was 0.93V, which is very close to Pt 20 wt%.

Furthermore, GSP 900 showed much better long-term stability and tolerance to crossover compared to Pt 20 wt%, as well as conducted ORR in a 4e-electron transfer pathway.

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