

# Nitrogen co-doped with fluorine on reduced graphene oxide for enhanced electrocatalytic activity and stability for ORR in alkaline fuel cells

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## Abstract

Nitrogen co-doped with fluorine on reduced graphene oxide (N-F-rGO) was prepared by one-pot hydrothermal treatment method. The scanning electron microscopy (SEM) images and X-ray photoelectron microscopy (XPS) spectra revealed the successful doping of nitrogen and fluorine into the rGO. The Brunauer-Emmett-Teller (BET) results demonstrated high surface area of N-F-rGO that are favorable for O<sub>2</sub> adsorption. The results show that N-F-rGO catalyst has improved the catalytic performance electrode for the ORR in alkaline environment than the fluorine undoped N-rGO. The Koutechy-Levich (KL) analysis and rotating ring disk electrode (RRDE) measurements suggest that N-F-rGO dominantly favors a 4e<sup>-</sup> reduction process. The nitrogen co-doped with fluorine on rGO exhibited remarkable long-term stability towards the ORR than Pt/C. These improved electrochemical properties indicate that N-F-rGO will be promising candidates for cost-effective electrode materials for application of non-polluting alternative energy sources.

**Keywords:** electrocatalyst, ORR, N-F-rGO, hydrothermal treatment, fuel cells

## 1. Introduction

The development of cost-effective, efficient and stable electrocatalysts towards oxygen reduction (ORR) has been aimed to overcome the bottleneck of widespread application of fuel cells (Ma, Ma et al. 2016). Pt-based nanomaterials show the greatest promise as electrocatalyst for this reaction among all current catalytic structures (Zhang, Shen et al. 2017). However, Pt-based catalysts are too expensive for making commercially viable fuel cells. The high cost, scarcity and lack of durability of traditional Pt-based electrocatalyst limits the widespread implementation of fuel cells for practical applications (Raj, Samanta et al. 2016). Therefore, the development of earth-abundant, cost-effective, stable, and catalytically active metal-free alternatives is highly desirable for application in renewable energy technologies (Hu, Xiao et al. 2018). While the progress in ORR catalyst has yielded some very attractive material designs, graphene has recently drawn the attention of scientists and engineers due to its some specific properties that can be fine-tuned for

electrocatalyst applications (Higgins, Zamani et al. 2016). Different notable methods have been developed to tailor the structure and fine-tune the surface chemistry of graphene which has impact in the field of electrolysis, whereby the properties of graphene and its composites have been shown to provide beneficial activity and stability enhancements for ORR. For these reasons, there is a large body of work done on graphene that has been doped with heteroatoms (Duan, Chen et al. 2015, Marinou, Răceanu et al. 2017). The performance of heteroatom-doped on graphene catalysts can be further improved through co-doping with different heteroatoms. This is due to the increased numbers of dopant heteroatoms and electronic interactions between different doped heteroatoms often generate additional synergistic effects than single heteroatom-doped counterparts (Zhang, Qu et al. 2016).

In this study, nitrogen was co-doped with the most electronegative element, fluorine, on reduced graphene oxide (rGO) via one-pot hydrothermal treatment method to enhance the stability and activity of ORR in alkaline fuel cells.

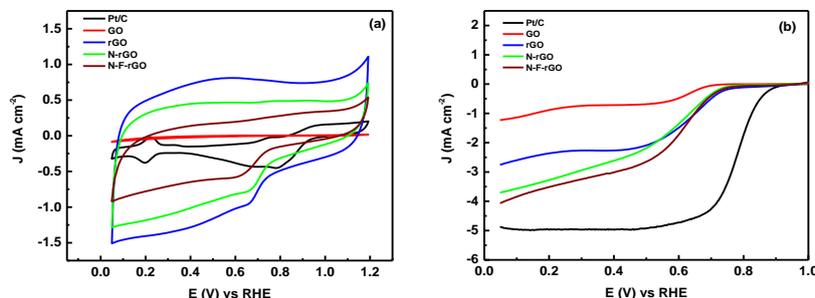
## 2. Methodology

Fluorine co-doped on reduced graphene oxide (N-F-rGO) were prepared by hydrothermal method. To evaluate the successful synthesis of the electrocatalysts, the scanning electron microscopy (SEM) images were obtained using Zeiss Gemini 500 scanning electron microscope, pore size distribution and specific surface area were obtained by Brunauer-Emmett-Teller (BET) using Micromeritics Tristar surface area and porosity analyzer, and X-ray photoelectron spectroscopy (XPS) measurements were done using Perkin Elmer PHI 5600 X-ray photoelectron spectrometer equipped with a monochromatic Al K $\alpha$  X-ray source. The electrochemical measurements were done by the triple electrode system using Autolab Metrohm PGSTAT128N potentiostat/galvanostat. The as-prepared electrode was used as the working electrode, while Hg/HgO and Pt wire were used as the reference and counter electrodes, respectively. The electrolyte was 0.1 M KOH aqueous solution.

### 3. Results and Discussion

#### 3.1. Physico-chemical Properties

The SEM morphologies of the as-prepared catalysts has shown of the images the randomly compacted and stacked of heteroatom (fluorine) doped on the crumpled platelets of graphene layers with more edges exposed. Furthermore, the BET specific surface area of N-F-rGO was  $103 \text{ m}^2 \text{ g}^{-1}$



**Figure 1.** (a) CV and (b) LSV curves of catalysts at 1600 rpm in  $\text{O}_2$ -saturated 0.1 M KOH.

#### 3.2 Electrochemical Properties

After the successful doping of N and co-doping with F onto rGO has been established, the electrochemical activity for ORR of the synthesized catalysts were investigated to gain insights of the ORR activity of the electrocatalysts. Both The cyclic voltammetry (CV) and linear swift voltammetry (LSV) measurements were carried out in an  $\text{O}_2$  saturated 0.1 M KOH solution. CV curves was obtained at a scan rate of  $20 \text{ mV s}^{-1}$  while LSV curves were obtained at a scan rate  $5 \text{ mV s}^{-1}$  and rotation rate of 1600 rpm. Similar CV and LSV curves were also obtained for GO, rGO and commercial 20% wt Pt/C for comparison.

**Figure 1 (a)** shows a well-defined single cathodic peak for rGO, N-rGO and N-F-rGO, which corresponds to the ORR. in  $\text{O}_2$  saturated solutions. However, it is shown that these ORR peaks is more intense with the with N-F-rGO than N-rGO. The observed ORR peak of N-F-rGO is at 0.63 V (vs RHE). The above results showed that N-F-rGO is more active for the ORR than and N-rGO. It is also shown in **Figure 1(b)** that N-F-rGO has better ORR catalytic performance than N-rGO. The N-F-rGO has an onset potential of 0.747 V (vs RHE) and limiting current density of  $-4.06 \text{ mA cm}^{-2}$ . This signifies that additional doping with F in N-F-rGO might have contributed to the improved catalytic performance of this material. This might be attributed to the high electronegativity of F atoms that induced polarization to adjacent atoms creating active sites to facilitate high ORR performance. The electron transfer number (n) per oxygen molecule was determined using Koutecky-Levich (K-L) equation. The peroxide yield as well as the electron transfer number (n) per oxygen molecules involved in the ORR were further determined by rotating ring disk electrode (RRDE) test. Both KL analysis and RRDE measurements have shown that electrocatalysts dominantly favor a 4e- reduction process. It is also estimated in RRDE measurements that N-F-rGO has  $\text{H}_2\text{O}_2$  percent yield between 22% and 34% over a potential range of 0.3 - 0.7 V (vs RHE).

The stability of electrocatalysts were evaluated by accelerated durability tests (ADT) with a potential cycling in a range of 0.6V - 1.15V in  $\text{O}_2$ -saturated 0.1 M

which is higher than nitrogen doped on reduced graphene oxide (N-rGO) only which is  $69 \text{ m}^2 \text{ g}^{-1}$ . This high value of surface area along with the wrinkles and disordered structure could have exposed more active sites that facilitated the adsorption of  $\text{O}_2$ , which would be advantageous for ORR applications. Furthermore, XPS results show that electrocatalysts were successfully synthesized by hydrothermal treatment process.

electrolyte. It was observed that after 5,000 cycles N-rGO and N-F-rGO did not show any significant change in LSV curves. This indicates that there's a negligible degradation of surface active sites with time. On the other hand, it is observed that Pt/C has decreased its limiting current in the LSV curve after 5,000 cycles indicating degradation of surface active sites with time.

### 4. Conclusion

The N co-doped with F on rGO were fabricated employing a one-pot hydrothermal treatment method was successfully prepared and confirmed by various characterization techniques such as SEM, XPS and BET. The N-F-rGO catalysts has shown an improved catalytic performance for the ORR in alkaline environment compare to N-rGO and rGO. Moreover, N-F-rGO exhibit a notable stability towards the ORR compared to the Pt/C in alkaline medium. The overall synergistic effect between N and F on rGO improved the ORR catalytic performance and durability of synthesized materials which indicates that N-F-rGO will be a promising candidate as electrode material for energy related applications such as the cost-effective manufacturing of fuel cells.

### References

- Duan, J., S. Chen, M. Jaroniec and S. Z. Qiao (2015). "Heteroatom-Doped Graphene-Based Materials for Energy-Relevant Electrocatalytic Processes." *ACS Catalysis* **5**(9): 5207-5234.
- Higgins, D., P. Zamani, A. Yu and Z. Chen (2016). "The application of graphene and its composites in oxygen reduction electrocatalysis: a perspective and review of recent progress." *Energy & Environmental Science* **9**(2): 357-390.
- Hu, C., Y. Xiao, Y. Zou and L. Dai (2018). "Carbon-Based Metal-Free Electrocatalysis for Energy Conversion, Energy Storage, and Environmental Protection." *Electrochemical Energy Reviews* **1**(1): 84-112.
- Ma, R., Y. Ma, Y. Dong and J.-M. Lee (2016). *Recent Advances in Heteroatom-Doped Graphene Materials as Efficient Electrocatalysts towards the Oxygen Reduction Reaction*.
- Marinoiu, A., M. Raceanu, E. Carcadea, M. Varlam, D. Balan, D. Ion-Ebrasu, I. Stefanescu and M. Enachescu (2017). "Iodine-Doped Graphene for Enhanced Electrocatalytic Oxygen Reduction Reaction in Proton Exchange

Membrane Fuel Cell Applications." Journal of Electrochemical Energy Conversion and Storage **14**(3): 031001-031001-031009.

Raj, C. R., A. Samanta, S. H. Noh, S. Mondal, T. Okajima and T. Ohsaka (2016). "Emerging new generation electrocatalysts for the oxygen reduction reaction." Journal of Materials Chemistry A **4**(29): 11156-11178.

Zhang, C., X. Shen, Y. Pan and Z. Peng (2017). "A review of Pt-based electrocatalysts for oxygen reduction reaction." Frontiers in Energy.

Zhang, J., L. Qu, G. Shi, J. Liu, J. Chen and L. Dai (2016). "N,P-Codoped Carbon Networks as Efficient Metal-free Bifunctional Catalysts for Oxygen Reduction and Hydrogen Evolution Reactions." Angewandte Chemie International Edition **55**(6): 2230-2234.