Direct synthesis of platinum group metal-free Fe-N-C catalyst for oxygen reduction reaction in alkaline media

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Abstract:

A direct, template-free synthesis of a novel, active Fe-N-C oxygen reduction reaction catalyst by the pyrolysis of ethylenediaminetetraacetic acid ferric sodium salt is demonstrated. Detailed physical characterization of the catalyst is carried out by surface area measurement, X-ray diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy in addition to electrochemical analysis using Rotating Ring Disk Electrode measurements. We study the effects of synthesis temperature on graphitization, surface area and their concurrent effects on the catalytic performance of the final products.

Keywords: Template-free; Ethylenediaminetetraacetic acid ferric sodium salt; Oxygen reduction reaction; Alkaline electrolyte; Graphitization.

1. Introduction

Oxygen electrocatalysis is crucial for developing fuel cell technology owing to the high usage of expensive platinum-based catalysts on the cathode and its relatively sluggish oxygen reduction reaction (ORR) kinetics. [1-5] Several alternative material systems with reduced or no Pt have been tested, but efforts to reduce the synthetic costs, improve performance and durability for industrial applications are ongoing. [3, 6-8] Fe-N-C systems, some of the most effective candidates to replace platinum have been synthesized in a variety of different ways, from graphene-based precursors and template-derived porous carbons to **template free systems**. [9-17] Most methods, however, involve tedious protocols which are difficult to scale up in a cost efficient manner on an industrial level.

In this work, we demonstrate a facile, one-step synthesis of a Fe-N-C system by the direct template-free pyrolysis of the low-cost bio-reagent, **ethylenediaminetetraacetic acid ferric sodium salt (EDTA-Fe-Na)** for high-performance ORR catalysis in alkaline electrolyte. Furthermore, we study the role and influence of temperature on graphitization, resulting surface area, doping levels and type of catalytically active centers on ORR catalytic performance. EDTA has previously been employed as a part precursor for pyrolysis and acid dehydration by some groups. [14] [18] [19] [20] A direct, template-free synthesis of an efficient Fe-N-C catalyst from an EDTA derivative is demonstrated for the first time.

2. Experimental

4 EDTA derived catalysts (EDCs), were prepared at different temperatures of the first heat treatment of commercially obtained precursor EDTA-Fe-Na. 6.5 g of EDTA-Fe-Na was pyrolyzed at: 950 °C (60 min) in N₂ (7at% H₂) gas (**EDC1**), 875 °C (60 min) in N₂ (7at% H₂) gas (**EDC2**), 800 °C (60 min) under a NH₃ gas flow (**EDC3**), 800 °C (60 mins) in N₂ (7at% H₂) gas (**EDC4**). The carbon product in each case was sonicated in dilute nitric acid and stirred overnight to remove metallic impurities. The product was then isolated by centrifugation, washed several times and dried. A second heat treatment was done in NH₃ gas for 60 min at 950 °C. Working electrodes were prepared by dropcasting standard inks (850 µL-DI: IPA and 150 µL-0.5 wt% Nafion) on a glassy carbon electrode. The catalyst loading was calculated to be 0.6 mg cm⁻². Standard Pt/C (10% ETEK, ~30 µg cm⁻²) was used for comparison. O₂ saturated 0.1 M KOH solution, **Hg/HgO (calibrated vs RHE) and Graphite rod were used as the electrolyte, reference and counter electrodes, respectively.**

3. Results and Discussions

Thermogravimetric analysis (TGA) (Figure 1a) in N₂ shows a ~10% weight loss up to 200 °C (H₂O content). A rapid ~50 wt.% loss is noted in the region of 200-400°C followed by a gradual 10-15 wt.% loss from, 400°C-750°C probably due to the decomposition of four -CH₂ groups (at wt. 56, ~15 wt %). Carbonization to different degrees occurs in the region of 750-950 °C. After washing in acid, the weight further decreases because of solvation of inorganic salts like Na₂CO₃ (formed by reaction of Na and COO⁻) and unreacted Fe compounds that form as by products. The final catalyst yield was observed to be ~1.5% by weight in each case.

X-ray Diffraction (XRD) (Figure 1b) of EDCs reveal the main characteristic peaks of h-graphite at 2θ values of 26.6 (002 plane), 42.8 (010), 43.6 (101), 54.5 (222) and 77.5 (110). The full width at half maximum (FWHM) of the XRD peaks is a parameter that reflects on factors like crystallite size, the degree of order, stress, and curvature of the graphitic planes. As a general rule, an increasing FWHM value is reflective of decreasing crystallite size. [21] Figure 1c shows the increasing FWHM values of the most intense 002 plane peak for catalysts from EDC1 to EDC4 indicating that EDC1 has a somewhat higher graphitic crystalline order as compared to EDC4 which has the least of the four catalysts. This difference can be explained by the fact that EDC1 has a higher synthesis temperature (950°C) than EDC4 (800°C) leading to a marginally higher graphitization. With increasing graphitization, the number of surface defects decreases and the surface area also shows a downward trend. [22, 23] It is widely known that commercially available crystalline graphite has a very low surface area as compared to amorphous activated carbon. EDC1 possesses the lowest value for the surface area (~148 m²/g) whereas EDC4 has the highest value (~218 m²/g). Most effective catalysts have high surface area contributed to by micropores which contain the active sites and mesopores which provide access of the electrolyte to the catalytic centers. An increasing surface area thus contributes to a better performance. [24, 25] Furthermore, it has been hypothesized that edge defects in graphene-based systems contribute to oxygen reduction reaction. [26,27,28]

Raman spectroscopy (Figure 1d) of the catalysts confirm the typical carbon identification peaks, defect induced D band at ~1337 cm⁻¹ and the sp² carbon signal at 1570 cm⁻¹ (G band). [29] The I_D: I_G ratio Raman spectra of EDC4 is seen to be the highest (~0.73) indicating the largest defect concentration of all the catalysts. This could be due factors like edge defects formed due to a low degree of graphitization and higher porosity in EDC4. The defect concentration of EDC3

decreases to ~0.47 consistent with an increase in graphitization. The lower the graphitic crystal order, the higher is the surface area and the better is oxygen reduction onset and half wave potential owing to the higher number of accessible catalytic sites.

Figure 1e demonstrates the LSV curves obtained from the rotating disk current for each of the EDCs. EDC4 shows the most positive ORR onset potential ~0.96 V and an impressive half wave potential ($E_{1/2}$) of ~0.8 V, an improvement over the commercial 10 wt% Pt/C catalyst (ETEK). EDC2 shows marginally better onset potential ~0.92 V over EDC3 (~0.88 V) and more positive $E_{1/2}$ (~30 mV). In spite of lower surface area of EDC2 as compared to EDC3, the improved performance can be attributed to more surface defects such as C_x-O_y and $C-N_x$ as further confirmed by XPS in this system. EDC1 shows the least activity in the process because of low N doping and least surface area due to higher graphitization. The ring current obtained from the peroxide oxidation is used to determine the peroxide percentage generated by the catalytic system. Peroxide is a catalytic poison, and it is generated when the ORR catalyst follows a 2-electron mechanism of reduction as opposed to a direct 4-electron pathway.

$$\%HO_2 = \frac{200 \times \frac{I_{ring}}{N}}{I_{disk} + \frac{I_{ring}}{N}} \dots\dots\dots (1)$$

where N= collection efficiency (0.43), I_{ring} = ring current, I_{disk} = disk current.

Figure 1f shows the peroxide percentage yields of the EDCs. EDC1 shows the highest average peroxide yield at different potential values. The low peroxide yields in the best catalysts indicate an efficient 4-electron transfer mechanism of ORR. Interestingly though, the lowest average peroxide yield is shown by EDC3. The precise reason is unclear and remains a matter of further study.

XPS of the EDCs reveal surface elemental composition (Table 1). The amount of nitrogen is between 0.5-0.8 % with EDC3 having the largest amount of nitrogen. The temperature of the first pyrolysis does not affect the amount of nitrogen, however, amount of iron detected goes from below detection limit for EDC1 sample and to 0.18 at. % for EDC4 sample. The N and Fe

content of EDC3 is higher because the first pyrolysis in NH_3 leads to efficient incorporation of nitrogen atoms and a probable increase in the stability of iron due to coordination with nitrogen.

The major effect that can be investigated using XPS is a study of carbon speciation, in particular, relative amounts of graphitic nitrogen and number of defects such as carbon-nitrogen and carbon surface oxides. Figure 2 (a-d) shows high resolution C 1s spectra curve fitted using multiple peaks due to graphitic nitrogen (284.4 eV), C-C and secondary carbons due to carbon coordinated to carbon-nitrogen and carbon-oxides (285 eV), C-N_x defects (286.2 eV), C-OH/C-OC (287.1eV), C=O (288 eV) and COOH (289.4 eV). Table 1 shows relative amounts (%) of graphitic nitrogen, C-N_x defects and the total amount of C-N_x and C_xO_y surface oxides in the carbon matrix. Samples EDC1 and EDC3 have the highest amount of graphitic carbon and the smallest amount of C-N_x defects and surface oxides. Samples EDC2 and EDC4 have smaller relative amount of graphitic carbon and larger amount of defects. EDC4 sample has the largest amount of C-N_x defects due to N doping.

The chemistry of nitrogen in the EDCs is described in Table 1 and in Figure 2 e-h. Imine like N occurs at ~397.6 eV, pyridinic-N at ~398.3 eV, N_x-Fe at ~399.5, pyrrolic at ~400.9 eV, graphitic N at ~402.1 eV and oxidized nitrogen species at binding energy higher than 403 eV. As the temperature of pyrolysis decreases, the nitrogen is getting reduced to higher relative amounts of pyrrolic and graphitic nitrogen. Sample heat treated in ammonia results in more oxidized nitrogen.

Fe 2p spectra shown in Figure 2 i-l along with TEM images shed more light into structure-to-property correlations. EDC1 sample has almost no Fe detected. As the temperature of the pyrolysis decreases Fe amounts increase. EDC2 sample has metallic Fe peak at 707.0 eV and Fe coordinated to nitrogen at 708.5 eV. Two other peaks at a higher binding energy between 710 and 713 are due to iron oxides which are also confirmed by broad satellite feature at 716.5 eV. At even lower temperatures of pyrolysis, EDC4 has mainly metallic iron peak and Fe-N_x centers. The presence of metallic particles is obvious from TEM images as well for this sample. Sample EDC3 heat treated in ammonia has largest amount of Fe detected and its chemical signature is very similar to that of EDC4.

There is no direct dependence of performance on the type of nitrogen present. We have demonstrated before that mechanisms of oxygen reduction in alkaline and acidic media are very different. In alkaline media no direct correlation between ORR performance and chemistry of

nitrogen is present. [30] A surface-independent outer-sphere electron transfer is promoted by the presence of surface hydroxyl groups rather than immediate involvement of N pyridinic and N-coordinated to iron sites in reaction. [31] Larger presence of defect sites in graphene network that are terminated in surface oxides and C-N defects for EDC4 and EDC2 samples facilitated ORR in alkaline media. Moreover, XPS analysis of Fe and high-resolution TEM images demonstrate that sample with the best performance has a higher amount of metallic particles. Even though EDC3 has lots of iron in the form of metallic particles, it does not cause better performance than that of EDC4 sample. The combination of lower density of defects sites and excess of iron particles results in much worse performance than EDC4.

4. Conclusions

We put forth a direct, facile, template-free synthesis of a novel Fe-N-C cathodic electrocatalyst from ethylenediaminetetraacetic acid ferric sodium salt. The effects of synthesis temperature on the catalytic structure in terms of graphitization, surface area and the subsequent influence on oxygen reduction catalysis in alkaline electrolyte has been explored. The best performing catalyst EDC4 has the lowest graphitization, highest surface area, highest defect concentration and an optimum level of doping and exhibits an improvement over the commercial Pt/C based catalyst.

Acknowledgement:

The authors would like to acknowledge Daihatsu Motor Company and US DOE for funding.

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Figure 1.

Figure 2.

Table 1.

Catalysts	N (at%)	Composition of N (Rel. %)					N-O (N6)	C (at%)	Composition of C (Rel.%)			Fe (at%)	O (at%)
		Imine (N1)	Pyridinic (N2)	N-Fe (N3)	Pyrrolic (N4)	Graphitic (N5)			Graphitic	C-N _x	C _x O _y + C-N _x		
EDC1	0.49	19.0	32.7	13.3	13.0	13.8	8.2	96.0	64.9	6.6	32.7	0.03	3.5
EDC2	0.42	14.6	34.2	19.1	19.6	9.6	2.9	95.0	60.9	7.9	37.2	0.08	4.4
EDC3	0.79	12.8	27.3	16.5	19.5	11.6	12.3	95.8	66.0	6.7	31.2	0.50	2.9
EDC4	0.50	9.2	25.4	15.2	27.0	14.0	9.2	94.9	57.1	12.5	40.0	0.18	4.4

Table 1. Elemental composition of all EDCs

Graphical Abstract