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

Rohan Gokhale, Yechuan Chen, Alexey Serov, Kateryna Artyushkova, Plamen Atanassov *

Center for Micro-Engineered Materials (CMEM), University of New Mexico, Albuquerque, NM -87106, USA

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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.

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 N_2 (7 at.% H_2) gas (EDC1), 875 °C (60 min) in N_2 (7 at.% H_2) gas (EDC2), 800 °C (60 min) under a NH_3 gas flow (EDC3), 800 °C (60 min) in N_2 (7 at.% H_2) 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 NH_3 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. O_2 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) (Fig. 1a) in N_2 shows a ~10% weight loss up to 200 °C (H_2O content). A rapid ~50 wt% loss is noted in the region of 200–400 °C followed by a gradual 10–15 wt% loss

* Corresponding author at: Department of Chemical and Biological Engineering, University of New Mexico, Albuquerque, NM-87106, USA.
E-mail address: plamen@unm.edu (P. Atanassov).

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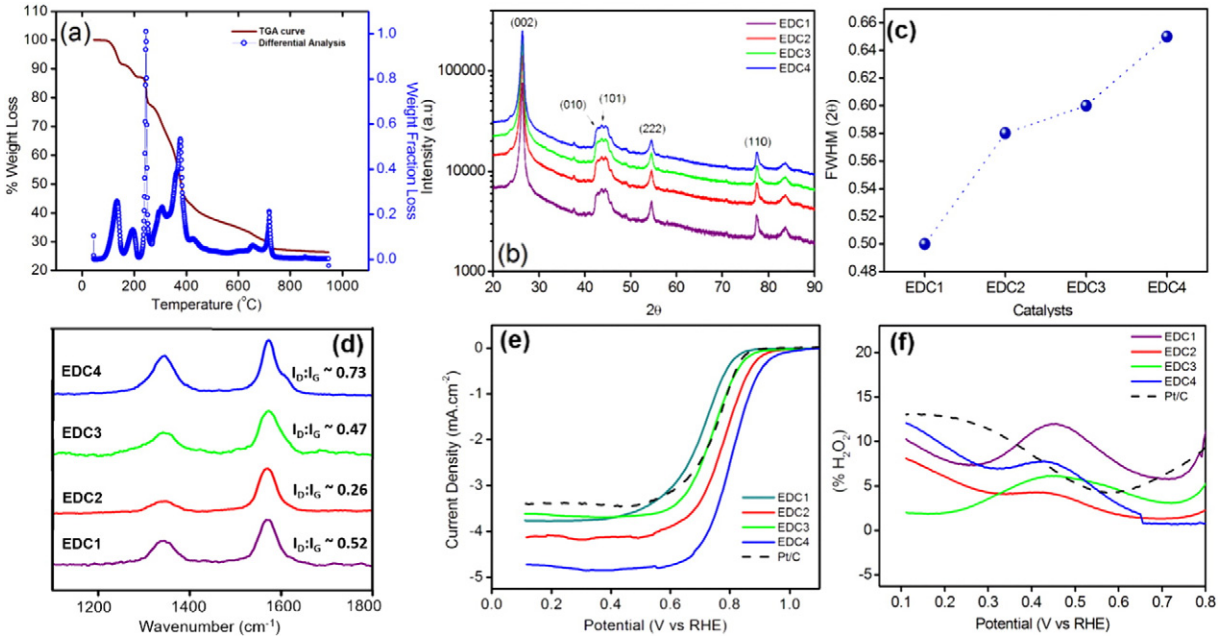

Fig. 1. (a) TGA and differential analysis of the precursor EDTA-Fe-Na (b) XRD of the catalysts (c) FWHM values for 002 peak in all catalysts (d) Raman spectra and the I_D:I_G values for all catalysts (e) LSV data for all catalysts in O_2 saturated 0.1 M KOH at 1600 rpm (f) % H_2O_2 produced for each catalyst at different potential values.

from, 400 °C–750 °C probably due to the decomposition of four —CH_2 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 Na_2CO_3 (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) (Fig. 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]. Fig. 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 m^2/g) whereas EDC4 has the highest value (~218 m^2/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 (Fig. 1d) of the catalysts confirm the typical carbon identification peaks, defect induced D band at ~1337 cm^{-1} and the sp^2 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.

Fig. 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 a 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.

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

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

Fig. 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 and 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