Research Paper

Nitrogen-Doped Carbon Foam as a Highly Durable Metal-Free Electrocatalyst for the Oxygen Reduction Reaction in Alkaline Solution

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ABSTRACT

Nitrogen-doped carbon foam (CF_N) with large surface area is synthesized via a template-free, scalable combustion technique using diethanolamine as a nitrogen source. The resulting macroporous, open-cell foam has micron-scale hollow cells, surrounded by thin, graphene-like walls. This material is applied as a metal-free electrocatalyst for the oxygen reduction reaction (ORR) in alkaline KOH solution. The activity of this metal-free electrocatalyst at the half-wave potential is just 43 mV lower than that of platinum-decorated carbon (Pt/CB), but 87 mV lower than a commercially available Fe-containing non-precious electrocatalyst (Pajarito Powder, PP), suggesting that iron is important in achieving the highest activities. In durability tests measured over 60,000 potential cycles, Pt/CB and PP undergo significant degradation, whilst the non-precious CF_N electrocatalyst shows negligible change, indicating high stability of the electrochemical active sites compared with platinum or iron. Such metal-free catalysts therefore show great promise as electrocatalysts for specific alkaline ion exchange membrane fuel cell (AEMFC) applications where long lifetimes are most important.

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1. Introduction

Fuel cells are electrochemical energy conversion devices that have attracted increasing attention due to their efficiency, versatility, and high power density. Polymer electrolyte membrane fuel cells (PEMFCs) have already been commercialized in residential stationary combined heat and power (CHP) units (Enefarm, Japan), as portable chargers for mobile devices (Upp, Intelligent Energy, UK), and in fuel cell vehicles (Toyota Mirai, Japan). One of the main drawbacks of PEMFCs is the high price. The kinetics of the oxygen reduction reaction (ORR) are slow at the cathode due to strong O=O bonding. Thus high platinum catalyst loading is required, increasing the cost. Another serious issue is durability. Carbon corrosion, Pt dissolution, nanoparticle ripening, and detachment all lead to deterioration in performance over time [1,2].

To overcome these issues, alternative electrocatalysts have been extensively explored. Non-precious metal ORR catalysts based on mixtures of iron, nitrogen and carbon have been studied since the 1960's in the quest to find an abundant and cheap electrocatalyst [3–10]. The synthesis of this class of Fe/C/N catalysts typically involves high temperature treatment of e.g. a transition metal-containing molecule mixed with a nitrogen-containing polymer binder, on a high surface area carbon support. Myriad variations on this basic recipe are frequently employed. The resulting electrocatalysts are essentially nanostructured nitrogen-doped carbons with varying transition metal content. The catalytic activity of Fe/C/N materials for the ORR is now surprisingly close to that of platinum-based electrocatalysts, and such catalysts are now commercially available (e.g. Pajarito Powder). Indeed, the US Department of Energy (DOE) has set specific targets for such non-precious metal catalysts to be used in vehicular applications,

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namely; 300 A/cm^3 volumetric activity at 0.80 V$_{iR-free}$ and 80° C, by 2017 [11,12].

However, such non-precious electrocatalysts still cannot compete with Pt in terms of activity or durability in the acid environment of PEMFCs [13]. In alkaline conditions the ORR is much faster, therefore such electrocatalysts are potentially much more applicable in alkaline anion exchange membrane fuel cells (AEMFCs) [14]. Whilst many AEMFCs still utilize precious metal electrocatalysts, attempts to use lower loadings or alternative metals have been made [15–17]. DOE targets for non-precious electrocatalysts in AEMFCs are: >350 mW/cm^2 power density at >80°C, for 2000 hours [18]. Nitrogen-doped carbons are very efficient electrocatalysts for the ORR in alkaline conditions [19,20]. To date nitrogen-doped carbon nanotubes [21]; mesoporous nitrogen doped carbon [22]; nitrogen-doped carbon black [23]; quantum dots [24]; metal-organic frameworks (MOFs); [25] and carbon nitride [26,27] have all been explored.

Graphene (and related materials) is also ideal for fuel cell applications [28,29], due to its large surface area, high conductivity, strength, and wide electrochemical potential window. Dai et al. pioneered the use of chemical vapor deposition (CVD)-grown nitrogen-doped graphene as an electrocatalyst for the ORR in alkaline medium, and observed improved current density compared with Pt/C [30]. However, thin films are not practical for large-scale electrocatalyst applications, and the Pt/C reference had unusually low activity. Sheng et al. synthesized nitrogen-doped graphene via thermal annealing of graphene oxide (GO) in the presence of melamine, resulting in high activity [31]. Sun et al. synthesized nitrogen-doped graphene by heating GO in ammonia, resulting in similar activity to Pt/C [32]. Indeed, in most studies, reduced graphene oxide (rGO) is utilized either as a precursor or support [19,33–35]. Restacking of the flat graphene sheets during processing can therefore lead to much lower accessible surface area for the ORR than expected for an isolated graphene sheet (2630 m^2/g). In order to prevent restacking and retain large surface area, a spacer (such as carbon nanotubes)[20] can be used between the graphene sheets, or the graphene can be assembled into a self-supporting foam-like structure, generally utilizing a sacrificial template. This approach has led to some of the best ORR activities reported to date [36]. However, currently there are very few rigorous studies on the durability of non-precious catalysts in alkaline media, although several groups have performed poisoning tests for methanol tolerance [22,27].

We have developed a technique to synthesize graphene-like carbon foam via combustion of sodium ethoxide in a relatively low cost, straightforward, template-free process. The resulting material has large surface area (up to 2600 m^2/g); has proven to be effective for hydrogen storage [37]; and is an efficient catalyst support [38,39]. By utilization of fluorine-containing alkoxide, we synthesized superhydrophobic carbons [40]. By doping the structure with nitrogen, we synthesized non-precious ORR electrocatalysts for use in acid environment [41–43]. Here, we apply nitrogen-doped carbon foam (CF$_N$) as a cathode electrocatalyst in alkaline medium; compare it with platinum-decorated carbon and a commercially available Fe/N/C catalyst (Pajarito Powder); and test their durability over 60,000 potential load cycles.

2. Experimental

Chemicals were used as received without further purification. Sodium, ethanol and platinum (II) acetylacetonate were obtained from Aldrich. Anhydrous ethanol, diethanolamine, 2-propanol, 5 wt.% Nafion dispersion solution and potassium hydroxide were purchased from Wako. Vulcan XC-72 (Cabot) carbon black (CB) was used as a platinum support. Reduced graphene oxide (rGO) was

purchased from GrapheneA. The non-precious catalyst (PP) was purchased from Pajarito Powder. Iron standard solution was 1000 mg/L and obtained from Aldrich. Deionized water was used in all cases.

Preparation of Nitrogen-Doped Carbon Foam (CF$_N$): Anhydrous ethanol and diethanolamine were blended in a suitable ratio and reacted with an equimolar amount of sodium in a sealed Teflon high-pressure reactor at 150°C for 24 h. The alkoxide product was transferred to a ceramic dish and ignited, burning with a steady yellow flame and decomposing to solid carbonized lumps. These were crushed, sonicated in deionized water, vacuum filtered, and then dried at 80°C under vacuum. Heat treatment was subsequently performed at 1000°C under N$_2$ flow for 2 h (75 sccm, 20°Cmin^{-1}), and then washed in deionized water. A second pyrolysis step was performed at 1000°C under 5% H$_2$ flow for 4 h (75 sccm, 20°Cmin^{-1}) to reduce the oxygen content. A final graphitization step was performed at 1400°C in N$_2$ for 15 hrs (200 sccm, 10°Cmin^{-1}) to improve conductivity [43]. The resulting sample is herein referred to as CF$_N$.

Preparation of Pt-decorated carbon black (Pt/CB): Pt/CB is used as reference electrocatalyst. Platinum (II) acetylacetonate dissolved in dichloromethane was slowly added to carbon black powder in an ultrasonic bath, and the solvent was removed via evaporation [44,45]. The product was transferred to an infrared furnace, and heated at 210°C for 3 h then 240°C for 3 h under N$_2$ flow, to decompose the platinum (II) to Pt metal nanoparticles. Pt/CB with 20 wt% Pt loading was obtained.

Materials Characterization: Materials were characterized by scanning electron microscopy (SEM, Hitachi S-5200, HD-2300A); X-ray photoelectron spectroscopy (XPS, ESCA-3400, Kratos Analytical Ltd.); Raman spectroscopy (Renishaw DM2500 M, argon-ion laser at 532 nm); and inductively coupled plasma—atomic emission spectrometry (ICP-AES) analysis (ICPE-9000, Shimadzu Corp.). Specific surface area was calculated by the BET nitrogen adsorption method (BELSORP-mini, BEL Japan, Inc.).

Electrode Preparation: Working electrodes were prepared according to Fuel Cell Commercialization Conference of Japan (FCCJ) guidelines [46]. The electrode was polished, then washed with deionized water in an ultrasonic bath for 10 min. CF$_N$ was dispersed in a mixture of deionized water, ethanol and 5 wt.% Nafion solution, in a volume ratio of 3:3:1, as optimized for Pt-free electrocatalysts [9]. In this work, the role of Nafion is only as a binder, and not an electrolyte material. For Pt/CB, 2-propanol was used in place of ethanol, and the ratio was 19:6:0.1, as optimized for Pt-based electrocatalysts [38]. The catalyst ink was homogenized for 30 min. 8 μl of the CF$_N$ ink (or 10 μL of Pt/CB) was carefully deposited onto the disk of a glassy carbon-disk Pt-ring electrode (0.196 cm^2, Hokuto Denko Corp.) then dried at 60°C for 15 min. A gold disk electrode was used for durability measurements (0.196 cm^2, Hokuto Denko Corp.) The resulting loading of CF$_N$ and PP on the electrode was 580 μgcm^{-2}. The loading of Pt on the electrode was 17.3 μgcm^{-2}.

Electrochemical Measurements: An automatic polarization system, rotating ring-disk electrode apparatus, and a three-electrode electrochemical cell (Hokuto Denko Corp.; HZ-5000, HR-500, and HX-107, respectively) were used. Pt wire and an Ag/AgCl electrode with saturated KCl were used as the counter and reference electrodes, respectively. Electrochemical experiments were performed in 0.1 M potassium hydroxide electrolyte saturated with O$_2$ or N$_2$ gas, at room temperature. Cyclic voltammograms (CVs) were obtained at a scan rate of 50 mVs^{-1} in N$_2$-saturated solution. All voltages are quoted with respect to the reversible hydrogen electrode (RHE) unless otherwise stated. Rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) measurements were performed in the range 1.17 to −0.03 V$_{RHE}$, at 10 mVs^{-1}, in O$_2$ saturated electrolyte at 400, 900, 1600, and 2500 rpm. For