Bio-inspired carbon electro-catalysts for the oxygen reduction reaction

Kathrin Preuss [a,b], Vasanth Kumar Kannuchamy [a], Adam Marinovic [a], Mark Isaacs [c],
Karen Wilson [c], Isaac Abrahams [b,d], Maria-Magdalena Titirici [a,b,*]

[a] School of Engineering and Materials Science, Queen Mary University of London, E1 4NS London, UK
[b] Materials Research Institute, Queen Mary University of London, E1 4NS London, UK
[c] European Bioenergy Research Institute, Aston University, B4 7ET Birmingham, UK
[d] School of Biological and Chemical Sciences, Queen Mary University of London, E1 4NS London, UK

ABSTRACT

We report the synthesis, characterisation and catalytic performance of two nature-inspired biomass-derived electro-catalysts for the oxygen reduction reaction in fuel cells. The catalysts were prepared via pyrolysis of a real food waste (lobster shells) or by mimicking the composition of lobster shells using chitin and $CaCO_3$ particles followed by acid washing. The simplified model of artificial lobster was prepared for better reproducibility. The calcium carbonate in both samples acts as a pore agent, creating increased surface area and pore volume, though considerably higher in artificial lobster samples due to the better homogeneity of the components. Various characterisation techniques revealed the presence of a considerable amount of hydroxyapatite left in the real lobster samples after acid washing and a low content of carbon (23%), nitrogen and sulphur (<1%), limiting the surface area to 23 m^2/g, and consequently resulting in rather poor catalytic activity. However, artificial lobster samples, with a surface area of ≈200 m^2/g and a nitrogen doping of 2%, showed a promising onset potential, very similar to a commercially available platinum catalyst, with better methanol tolerance, though with lower stability in long time testing over 10,000 s.

1. Introduction

The increasing trend in oil price, concerns about energy security and the need for improvement of hydrogen infrastructure has sparked a flurry of research into the technological aspects of its production and distribution. Fuel cells are considered as one of the most promising technologies, providing clean and sustainable energy. A fuel cell's efficiency is mainly dictated by the efficiency of the catalyst for the oxygen reduction reaction (ORR), which occurs at the cathode of the fuel cell. Up to this point, platinum supported on carbon materials has proven to be the best catalyst for the ORR, though certain shortcomings still limit the large-scale commercialisation of fuel cells. The rather slow ORR kinetics and low durability/stability in terms of long term usage as well as the very limited resource of platinum and thus the high cost make the accessibility of this technology limited [1,2]. Hence, there is a high demand for alternative inexpensive catalyst materials, with good ORR performance similar to platinum.

Carbon based materials are considered as promising alternative candidates due to their excellent electronic and mass transport properties [3], which are essential for the ORR process. Within this context, nitrogen doped carbons have become popular and are often reported as very well performing ORR catalysts [4]. Theoretically, the electronic transport properties and thus the ORR efficiency of the carbon material depend on the nature of the nitrogen moiety incorporated in the carbon framework [5,6]. The majority of studies have involved incorporation of nitrogen atoms either via in situ doping [7–9], or by the post-treatment of an already synthesised carbon material [10,11]. In situ doping has proven to be the preferential route to obtain homogeneously distributed nitrogen atoms in the carbon framework. To achieve this, usually a nitrogen source is introduced in the synthesis process along with the carbon source [7,12], sometimes also in the presence of an activation agent or pore generating compound (inorganic salts) [13,14], at elevated temperatures. The activation agent or "template" is usually added to create high surface area and pore volume, which are both essential features for the ORR [15]. Synthesising ORR catalysts from biomass is a further improvement, as it can make the process more sustainable and considerably reduce the production costs.

The second most abundant biomass after cellulose as well as the most abundant nitrogen containing compound in nature is

---

chitin [16]. Chitin can be found in crustacean shells as the main component together with calcium carbonate, which is needed for strengthening, aside from various proteins [16]. The worldwide consumption of crustaceans in 2013 alone was 13 Mt [17], making chitin, as well as its deacetylated derivative chitosan readily available biomass sources for various applications, such as water treatment, pharmaceutical or cosmetic products and plant protection [18].

Several catalysts for electrochemical applications synthesised from chitin and chitosan have been reported in the literature with promising features for the ORR. Yuan et al. [19] carried out hydrothermal carbonisation of pure chitin mixed with water followed by high temperature activation with $ZnCl_2$, resulting in carbon sheets with a very similar onset potential to standard platinum in alkaline media. Li et al. [20] synthesised a chitin aerogel from shrimp shells via various acidic and alkaline washing steps, followed by pyrolysis, which showed an even slightly more positive onset potential than commercial platinum on carbon, with an impressive stability and methanol tolerance. Wu et al. [21] used chitosan as a starting material in a two-step process, where first chitosan and acetic acid were hydrothermally carbonised followed by pyrolysis. The catalytic performance was similar to that for the chitin aerogel [20]. Additionally Wu et al. co-doped their catalyst with sulphur, which led to a further increase in activity and to an identical onset potential to the platinum standard. Nitrogen doped carbon nanosheets with good catalytic activity in alkaline media have also been synthesised from a chitosan and melamine mixture with a pyrolysis process followed by KOH activation [22]. Wu et al. [23] synthesised a catalyst from pure chitosan with rather low catalytic activity, that showed excellent performance and stability when a cobalt salt was added during the synthesis process, resulting in an interconnected nitrogen doped carbon framework with Co/Co_3O_4 nanoparticles. A different approach was taken by Aghabarari et al. [24], who used a chitosan derivative mixed with carbon black as support for platinum particles to show enhanced catalytic activity compared to the commercial platinum supported on carbon black.

Though a considerable amount of research has been carried out in the field of catalysts made from chitin and chitosan, our aim was to find an easy and straightforward one-pot approach, without the need for several process steps or harsh chemicals. Herein we report the synthesis of a catalyst made purely from food waste, i.e. lobster shells taken from the lobster's carapace, as this part contains the largest amount of chitin, in relation to calcium carbonate [25]. However, a particular concern when using real biomass is the reproducibility in the resulting materials due to the very heterogeneous structure of the biomass (i.e. not all lobster shells contain the same type and amount of chitin and $CaCO_3$). Therefore, a simplified version of artificial lobster shell, made of chitin and calcium carbonate, was also synthesised and tested as a catalyst for ORR for comparison.

2. Experimental

2.1. Catalyst synthesis

All chemicals were used as received from Sigma Aldrich in pure form. Frozen lobster shells (*Homarus americanus*) taken from the animals' abdomen after consumption of the lobster meat, were used to produce the lobster catalyst (abbr. L). A paste made out of 1.5 g Chitin and 0.5 g $CaCO_3$ with 7 mL of deionized water, which was dried at room temperature overnight, represents the simplified artificial lobster (abbr. AL). Both catalysts were weighed into ceramic crucibles, closed with a ceramic lid and placed in a Carbolite high temperature furnace, followed by flushing with nitrogen for 30 min. The carbonisation was carried out under inert atmosphere

with a heating rate of 3 °C/min up to 1000 °C, where the temperature was kept for 4 h. The samples were then allowed to cool to room temperature under inert atmosphere. To remove residues like calcium carbonate from both samples, washing in 3 M acetic acid was performed, by stirring for 24 h, followed by rinsing with deionized water over vacuum filtration and freeze drying for 48 h.

2.2. Catalyst characterisation

Electron micrograph images were obtained with a FEI Quanta 3D Scanning Electron Microscope (SEM), including Energy-dispersive X-ray spectroscopy (EDS), and a JEOL JEM-2010 Transmission Electron Microscope (TEM). Elemental Analysis of C, H, N and S was performed with a Thermo Flash 2000 analyser fitted with a Cu/CuO CHNS column and a TCD detector, calibrated to sulphanilamide. Functional surface groups were specified via X-ray Photoelectron Spectroscopy (XPS) using a Kratos Axis HSi XP spectrophotometer equipped with a charge neutraliser and a monochromated Al $K\alpha$ source (1486.7 eV). Spectra were recorded at normal emission using a pass energy of 40 eV under a vacuum of 10^{-10} Torr. Surface area and pore size distribution were determined with Brunauer–Emmett–Teller (BET) theory and Quenched Solid Density Functional Theory (QSDFT), respectively, using nitrogen absorption and desorption isotherms obtained at 77 K with a Quantachrome Nova 4200e. Thermogravimetric analysis (TGA) was carried out on a TA Instruments Q500 with a heating rate of 10 °C/min up to 1000 °C in Air. Raman spectroscopy was performed with a Renishaw Raman microscope with a helium neon laser at 633 nm.

Electrochemical testing was performed with a rotating (RDE) and a rotating ring (RRDE) disk electrode on a Metrohm Multi Autolab M101. A three-electrode configuration with Ag/AgCl as reference electrode and platinum as counter electrode was used, as well as a 3 mm diameter glassy carbon (GC) working electrode for RDE and a 5 mm diameter GC disk with platinum ring for RRDE, respectively. Samples were tested in alkaline and acidic media at room temperature, using 0.1 M KOH and 0.5 M H_2SO_4, respectively. The samples' performance was compared to a commercially available platinum standard from Sigma Aldrich (20 wt% platinum on Vulcan carbon). The mass loading for the synthesised catalysts on the electrodes was kept at 212 μg/cm^2 and 107 μg/cm^2 for the platinum standard. Testing was performed by Cyclic voltammetry (CV) at a scan rate of 100 mV/s was run after first purging the electrolyte with N_2 for 30 min. This was followed by purging with O_2 for another 30 min and subsequently carrying out CV and Linear Sweep Voltammetry (LSV) at a scan rate of 10 mV/s for rotation speeds ranging between 400 and 2400 rpm. For stability/durability testing a chronoamperic profile was run for 10,000 s, where a constant potential of –0.25 V was applied at a constant rotational speed of 800 rpm and the change in current was recorded. To check the samples' tolerance to methanol, a chronoamperic profile was run, where 5 mL of methanol was added to the electrolyte after 160 s. For the electrochemical testing an ink of each catalyst was prepared by dissolving either 3 mg for the synthesised catalysts or 1.5 mg of the platinum standard in 100 μL Nafion (5% w/w in water and 1-propanol, Alfa Aesar) and 900 μL deionized H_2O, leaving the mixture to sonicate for at least 30 min to ensure homogenisation. Subsequently 5 μL (RDE, electrode area 0.071 cm^2) or 14 μL (RRDE, electrode area 0.196 cm^2) of the ink was carefully pipetted on the working electrode and dried at room temperature.

Electron transfer numbers for the RDE were calculated by the Koutecky–Levich equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_l} = \frac{1}{nFAkC} + \frac{1}{0.62nFAD^{\frac{2}{3}}\omega^{\frac{1}{2}}\nu^{-\frac{1}{6}}C}$$