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Highly efficient nitrogen-doped carbide-derived carbon materials for oxygen reduction reaction in alkaline media

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ABSTRACT

In this work, a novel type of nitrogen-doped carbide-derived carbon (N-CDC) catalysts is synthesized and their activity toward the oxygen reduction reaction (ORR) is investigated. Two different methods of preparation of N-CDC materials are compared: chlorination of titanium carbonitride and pyrolysis in the presence of a nitrogen-containing compound (dicyandiamide) of pre-chlorinated titanium carbide. The obtained catalysts are tested for ORR activity in 0.1 M KOH solution using the rotating disk electrode method along with their stability during 1000 cycles and compared to a commercial Pt/C catalyst. The surface morphology is investigated using scanning electron microscopy and the bulk composition with energy dispersive X-ray spectroscopy. The surface composition of the catalyst materials is analyzed with X-ray photoelectron spectroscopy and the structure with X-ray diffraction and Raman spectroscopy. The porosity of N-CDC materials is described with N_2 physisorption. The dicyandiamide-derived N-doped CDC material showed excellent electrocatalytic activity for ORR in alkaline media. This N-CDC catalyst could be considered as a promising cathode material in alkaline fuel cells.

1. Introduction

The oxygen reduction reaction (ORR) is one of the most important electrochemical reactions, used in metal-air type batteries [1] and different types of fuel cells [2–5]. Various carbon nanostructures have been widely used as support materials for precious metal catalysts due to their high electrical conductivity, porosity and stability in electrochemical conditions. Owing to their porous structure, reactants and products are easily transferred to and from the active sites. Carbon nanomaterials can also be doped by heteroatoms, most commonly nitrogen [6–12], thereby increasing their electrocatalytic activity toward the ORR [13]. The most efficient N-doped carbon catalysts usually fall into two groups, those incorporating both nitrogen and a transition metal [12,14–16] or simply nitrogen heteroatoms into a carbon matrix [17]. By introducing electron-rich nitrogen atoms into the carbon support, the π electrons in carbon are conjugated to the lone-pair electrons of nitrogen atom [18]. The effect of nitrogen doping depends highly on the placement of the dopant atoms in the carbon lattice [7,18]. Reportedly there are four different types of nitrogen species in carbon-based nanomaterials, pyridinic-N, pyrrolic-N, quaternary-N (graphitic-N), and pyridinic $N^{+}–O^{-}$. Recently, the quaternary-N sites have been further divided into two separate types depending on their exact position in the carbon lattice [19]. The ORR can proceed by two pathways, a two-electron route, which forms hydrogen peroxide as an intermediate and can thus be used for H_2O_2 production, and a four-electron route, which is more desirable in fuel cells and metal-air batteries. Pyridinic-N is reportedly responsible for donating one *p*-electron to the aromatic π-systems, thereby increasing the electron-donor ability of the material and thus its electrocatalytic activity by promoting the four-electron pathway [9,20]. However, it has also been found that increasing the percentage of graphitic-N by thermal annealing increases the overall ORR activity of N-doped carbon materials [21] and there are even some studies that suggest pyridinic-N promotes the 2-electron pathway instead [22], thus there is no

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consensus as of yet regarding the role played by the N dopant in ORR electrocatalysis.

Another important factor determining the ORR activity of N-doped carbons is the amount of nitrogen both on the surface and in the bulk of the material. Surface concentration of nitrogen up to 8.4% were shown by Rao et al. to increase the ORR electrocatalytic activity in acidic solutions [23]. In alkaline conditions, similar results have been found [24,25], suggesting that the number of active sites for both alkaline and acidic O_2 cleavage rises as the surface nitrogen content increases. The increase of bulk nitrogen has been shown to have an effect on the valence and conductive bands near the Fermi level, resulting in metallic conductivity [26,27], which in turn increases the catalytic activity as the speed of electron transport rises.

There have been a number of methods developed to synthesize nitrogen-doped carbon-based catalysts, for example post-synthesis doping by thermal treatment of a carbon material in the presence of a nitrogen source [11,28,29] or in-situ doping by chemical vapor deposition [6,30], laser ablation [31] and solvothermal methods [2]. Pyrolysis of a carbon material along with cheap nitrogen precursor is an extremely cost-effective method for synthesizing large amounts of active materials. For such synthesis, a number of substances have been tested [10,11,13,28,32] with dicyandiamide (DCDA) emerging as the most promising for facile one-step synthesis [29,33]. Nitrogen doping has been undertaken for a multitude of carbon materials, such as graphene [6,8,29,34], carbon nanotubes [11,18,20,30,35,36] and nanofibers [37], carbon aerogels [38–40] and different types of mesoporous carbon [17,41–43].

Porous carbons have traditionally been used as a support material for catalytic metal nanoparticles, such as Pt [44]. However, the properties that make them a good support material, such as stability in both alkaline and acidic conditions, high specific surface area and easily modifiable surface, also make them attractive as a base material for nitrogen doping [42,43]. Among these materials, carbide-derived carbon (CDC), which is a carbon material produced by removing the non-carbon atoms from a carbide lattice, stands out as an exceptional way to gain a base material with tunable properties [45]. The specific surface areas of CDC materials are typically around 1000–2000 $m^2\ g^{-1}$, the pore size is easily tunable via selection of different starting materials and synthesis temperature [46,47] with reproducible results in large scales [48]. This allows one to obtain highly optimized base carbon materials for further nitrogen doping. The most common procedure uses thermo-chemical treatment of carbide powder in chlorine gas flow at high temperature. Depending on the chemical composition of the carbide, but also of the desired porosity and nanostructure of the target CDC, the synthesis temperature can be varied in between 300 and 1100 °C [49,50]. Chlorination temperatures above 1200 °C tend to yield turbostratic low-surface area carbon materials, which usually offer less interest for energy related applications. Recently, there have been also studies about the ORR activity of un-chlorinated carbonitrides [51] and undoped CDC materials [52–54].

In this study, we show a simple approach to synthesize a novel type of highly active nitrogen-doped carbon catalyst from carbide-derived carbon and compare it to a commercially used chlorination process to achieve nitrogen-doped CDC materials. DCDA is used as the nitrogen source in a pyrolysis procedure [29,33,55] to introduce nitrogen moieties into the highly porous CDC network and enhance the ORR activity of the materials. The activity of these catalysts is compared to a carbonitride-derived material and commercial Pt/C and a variety of physical properties of the catalysts are studied to relate them to electrocatalytic properties.

2. Experimental

2.1. Materials and catalysts preparation

2.1.1. Preparation of nitrogen-doped catalysts from carbides and DCDA

Micro/mesoporous CDC samples 1094 and 13 with BET surface area of 1993 $m^2\ g^{-1}$ and 1889 $m^2\ g^{-1}$, respectively, purchased from Skeleton Technologies OÜ (Estonia), were made from titanium carbide using chlorination procedure described elsewhere [56]. To reduce the grain size of the materials, the CDC materials were ball-milled using 5 mm ZrO_2 balls. The material was weighed into a ball-milling container and ethanol was added to achieve a motor-oil like viscosity. Polyvinylpyrrolidone, a surface-active agent, was also added in an amount according to 1/10 of the carbon material to enhance the ball-milling process. The catalysts were ball-milled for 1 h. To the CDC material, 20 times the weight of the carbon material of dicyandiamide (DCDA) was added. The dispersion was sonicated for 2 h to achieve a homogeneous mixture and dried in vacuum at 75 °C. The material was collected into a quartz boat and pyrolyzed in a flowing nitrogen atmosphere at 800 °C for 2 h using a heating rate of 10 °C min^{-1}. After that the furnace was slowly cooled to room temperature and the products were collected and weighed. This procedure for N-doping has been optimized in previous works [29,33,55].

2.1.2. Preparation of a nitrogen-doped catalyst from titanium carbonitride

For synthesizing the 040-N material, titanium carbonitride powder ($TiC_{0.5}N_{0.5}$, H.C. Starck, Lot. 75624, 150 g) was treated with chlorine gas (AGA, 2.8) in a horizontal tubular quartz furnace at 800 °C for 4 h. The flow-rate of chlorine was 2.5 l min^{-1}. The gaseous titanium tetrachloride produced during the chlorination process was neutralized in an alkaline solution. During heat-up and cooling the reactor was purged with argon. The produced carbon powder was additionally purified in a hydrogen flow at 800 °C during 2.5 h to remove all the chlorine residues left in the carbon material. The overall yield of the process was 5.1 g of the nitrogen-doped porous carbon powder.

2.2. Surface and porosity characterization

Helios TM NanoLab 600 (FEI) was used to provide scanning electron microscopy (SEM) images of catalysts. The catalyst materials were suspended in ethanol and pipetted onto a polished glassy carbon (GC) substrate. Various areas were studied using a lower magnification to learn the characteristics of the material and the microstructure of the catalysts was investigated using a higher magnification. The elemental concentration profile was determined using energy-dispersive X-ray (EDX) microanalysis via Helios NanoLab 600 electron-ion dual beam microscope equipped with 50 mm^2 X-Max SDD detector (Oxford Instruments). The energy of primary electrons was 10 keV. The spectra were analyzed by using the standard procedures provided by INCA software (Oxford Instruments).

For obtaining the surface composition of N-doped catalysts, X-ray photoelectron spectroscopy (XPS) was used. The N-CDC materials were dispersed in ethanol at a concentration of 2 mg ml^{-1} and pipetted onto polished glassy carbon plates (1.1 × 1.1 cm). For removing the solvent, the plates were heated in an oven at 80 °C. The SCIENTA SES-100 spectrometer was employed for carrying out the XPS analysis. The catalysts were examined with a non-monochromatic twin anode X-ray tube (XR3E2), where the characteristic energies were 1253.6 eV (Mg $K\alpha_{1,2}$, FWHM 0.68 eV) and 1486.6 eV (Al $K\alpha_{1,2}$, FWHM 0.83 eV). The pressure in the analysis