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Coating procedure for chemical and morphological functionalization of multilayer-graphene foams

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ABSTRACT

A new strategy for designing the morphology and the chemical/physical properties of carbon structures is developed by functionalization of porous carbon templates. In a thermal decomposition procedure self-prepared multilayer-graphene foams (GF) are coated with a nitrogen-containing carbon layer (NCL) which has a porous structure. The use of a nitrogen rich ionic liquid as precursor generates a NCL with a very high nitrogen level of 35.3 wt%. To the best of our knowledge, this is the first synthesis of a hierarchical structured N-GF with such a high nitrogen amount. Structural studies on the NCL confirm C_5N and C_3N_4 species. Compared to uncoated GF it could be demonstrated that the functionalized porous carbon template (N-GF) has an increased electronic conductivity and electrochemical stability. Electrochemical characterizations of polymer electrolyte membrane fuel cells (PEMFC) prepared with Pt catalysts supported on N-GF show an increased performance which is attributed to improved mass transport properties and higher electronic conductivity of the porous composite material. Morphological, structural, chemical, and electrochemical characterizations were performed.

1. Introduction

Carbon nanostructures are key components for a large number of technical applications, especially in the field of energy generation or storage. For these applications high electronic conductivity, electrochemical stability and good mass transport properties for gases or liquids are among the most desirable material properties.

With respect to these three points many carbon materials have been developed in the past. Various methods [1–3] for preparation of high-surface-area carbon [4–8] are known, for instance chemical and physical processes, catalytic activation of carbon precursors [9], carbonization of polymer blends containing thermally decomposable components and carbonization of polymer aerogels. Methods for the preparation of carbon foams with a controlled pore size distribution and an extremely high surface area (up to 4100 $m^2 g^{-1}$) make use of various hard and soft templating approaches [10–13]; however, most of the templates are expensive and difficult to produce.

The active area of a foam material can be increased by formation of a hierarchical pore structure. It was reported in literature that hierarchical porous carbon systems can be prepared by template-directed CVD or template assembly methods [14–17]. The disadvantage of this CVD procedure is a very elaborate processing including expensive equipment and several etching steps. Otherwise, hierarchical GFs can be easily synthesized by a vesicant-assisted foaming method or a directional freezing method [18].

Compared to undoped carbon materials, heteroatom (N, P, B) doped [19–21] carbon species are known for an improved electronic conductivity and catalytic activity [22,23]. To incorporate N-atoms into carbon lattices, various methods have been developed, e.g. chemical vapor deposition [24], thermal annealing of carbon structures in NH_3 atmospheres [25], arc discharge processes with pyridine/NH_3, carbonization of natural carbon sources (e.g. egg white protein), or nitrogen plasma treatment [26]. Recently a synthesis route for samples with a high nitrogen content of 11.2 wt% was reported [27].

An increased conductivity by nitrogen doping of carbon combined with a hierarchical structure has been explored as a

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promising route for improving the catalytic performance [28–31]. Guo et al. synthesized nitrogen doped hierarchical porous carbon foams by pyrolyzing nitrogen-rich conductive polymers under argon atmosphere [32]. Samples with a low nitrogen doping content of 0.31–1.77 at% could be achieved by this process. It was also demonstrated for heteroatom doped carbon materials, including nitrogen, phosphor, boron or sulphur doped carbon nanotubes or graphene that these materials exhibit a high electrochemical stability and an efficient catalytic activity for oxygen reduction reactions (ORR) [33–36].

In the present study, we report a versatile and scalable synthesis for preparation of a porous carbon composite consisting of a multilayer-graphene foam coated with a nitrogen-containing carbon layer. Fig. 1a illustrates the architecture and Fig. 1b the preparation route of the composite. In a first preparation step macro-/microporous GF was produced by an optimized pyrolytic decomposition of sodium ethoxide (NaOEt). The subsequent coating process was performed by thermal decomposition of an ionic liquid in the GF substrate. Compared to pure GF it could be demonstrated that the N-GF has an increased stability, electronic conductivity and also very good mass transport behaviour for gases.

2. Experimental

2.1. Materials

Sodium ethoxide (95%, Sigma-Aldrich, Munich, Germany) is used as a precursor for GF, while for the NCL 1-ethyl-3-methylimidazolium dicyanamide (EMIM-dca, BASF AG, Ludwigshafen, Germany) is used as precursor. The catalysts were prepared by electrochemical reduction of hexachloroplatinic acid (40 wt% Pt, $H_2PtCl_6 \cdot 6H_2O$, Umicore, Hanau, Germany) dissolved in a Nafion® solution (20 wt%, DuPont, Delaware, USA) containing polytetrafluoroethylene particles (PTFE, Sigma-Aldrich, Munich, Germany) and the prepared GF and N-GF catalyst support.

2.2. Preparation of GF and N-GF

The functionalized carbon structure was prepared in a three step procedure, illustrated in Fig. 1b. In step 1, 1 g of NaOEt was decomposed at 800 °C for 1 min in a small furnace which is preheated at the desired temperature. After 1 min the resulting GF-product (0.63 g) was immediately removed from the oven, cooled down to ambient temperature, crushed to fine powder and washed (with centrifugation) in deionized water to remove residual side products. Finally the samples were dried at 80 °C. In step 2 the prepared GF was impregnated with EMIM-dca followed by a second heating process at 600 °C for 1 min under ambient atmosphere (step 3). The influence of the heating temperature and the IL content on the product composition was optimized in a temperature range between 550 and 800 °C (see Table 1). Afterwards, the products were characterized by physical and chemical techniques as described in Section 2.3.

2.3. Characterization of GF and N-GF

Transmission electron microscopy (TEM) pictures were taken with a JSM 6400F instrument (Jeol, Munich, Germany). Samples were suspended in ethanol and applied on a TEM grid. The samples were also measured by scanning electron microscopy (SEM) with a JXA-840A (Jeol, Akishima-Shi, Japan) and Helios NanoLab™ 600 microscope (FEI, Eindhoven, The Netherlands).

The elemental analysis was carried out on a CHN Vario EL3 (Elementar Analysensysteme GmbH, Germany) instrument. The samples were combusted in a pure oxygen atmosphere and the resulting products were analyzed by thermal conductivity detection analysis (TCD) with respect to NO_2, CO_2 and H_2O.

The Raman spectra were recorded with a Renishaw InVia Reflex micro-Raman system (Renishaw, Gloucestershire, UK) with a frequency doubled He:Ne laser (633 nm) as excitation source. The sample surface was measured with a laser power of 17 mW.

For characterization of the surface area N_2 adsorption–desorption–measurements at 77.3 K were performed according to Brunauer–Emmett–Teller (BET) on an ASAP 2010 volumetric adsorption analyzer (Micromeretics, Norcross, USA). The samples were degassed at 100 °C for 10 h under vacuum before the test. The specific surface area was determined in a relative pressure range of 0.05–0.2.

Thermo Scientific VG ESCALAB250 spectrometer (Thermo Scientific VG, East Grinstead, UK) with a monochromatic AlKα-source (1486.6 eV, 15 kV, 250 W) was used to obtain X-ray photoelectron spectroscopy (XPS). The XPS energy scale was calibrated by setting the binding energy of the carbon support to exactly 284.6 eV referenced to the Fermi level. The deconvolutions of the XPS spectra were carried out using CasaXPS software.

2.4. Conductivity and stability tests

Electrochemical impedance spectroscopy (EIS) measurements were taken with a Zennium workstation (Zahner-Elektrik GmbH & Co.KG, Germany) in galvanostatic mode (DC current density: 0 A cm^{-2}, AC amplitude of 100 μA cm^{-2}). Nyquist plots were recorded from 100 kHz to 100 mHz in N_2-saturated $HClO_4$ (0.1 M). A working electrode was prepared as follows: prior to each experiment a glassy carbon disk electrode (diameter: 1.5 mm) was polished with 0.05 mm alumina suspension and cleaned with deionized water. 42 μg GF or N-GF was dispersed in deionized water and coated onto the glassy carbon electrode. Then, 57 μL cm^{-2} of 100-folds diluted 5 wt% Nafion® solution (Ion Power Inc., Buckinghamshire, UK) in distilled water was dropped onto the carbon layer. Two glassy carbon disc electrodes are used, the one - two times coated and measured with GF (2 samples) and the other - two times with N-GF (2 samples). The two electrodes were also measured prior to each coating. Only the averaged data of 2 samples per GF, 2 samples per N-GF and 2 measurements of each of the two uncoated electrodes are presented. The maximum difference in the resistance between two samples of the same GF, N-GF coated electrodes and the uncoated electrodes was below 1%, a strong indication for the credibility of the results. For measuring the electrochemical stability an accelerated aging protocol was used according to Meier et al. [37]. Details of the test procedure are given in Section 4 of the supporting information. This method measures the electrochemical surface area (ECSA) by hydrogen adsorption/desorption CV measurements (0.05–1.1 V, 20 mV s^{-1}, 0.1 M $HClO_4$).

2.5. MEA preparation and characterization by polarization measurements

For MEA testing platinum catalysts supported on GF, N-GF and different carbon supports (Supplementary material Section 1.2.) were used. The platinum loading of Pt@GF or Pt@N-GF powders is 32.2 wt% and 7.7 wt%, respectively. The final MEA consists of the self-made anode (details of the catalyst preparation and characterization can be found in 1.2 and 1.3 of the supporting information), a commercial cathode (ELE0162, Johnson Matthey Royston, London, UK) with a platinum loading of 0.4 mgPt cm^{-2} and a Nafion 212 (DuPont, Delaware, USA) membrane. The final geometric area is 12 cm^2 (3.5 × 3.5 cm^2). The MEAs were prepared by hot-pressing at 125 °C with a pressure of 0.5 kN cm^{-2} for 6 min.

MEAs were tested in a Biologic fuel cell test station (Bio-Logic,