Performance of Polymer Electrolyte Membrane Fuel Cell Single Cells Prepared Using Hierarchical Microporous-Mesoporous Carbon Supported Pt Nanoparticles Activated Catalysts

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ABSTRACT

Hierarchical microporous-mesoporous carbon supports were prepared from molybdenum carbide using the high temperature chlorination method at six different synthesis temperatures within the range from 600 °C to 1000 °C. The platinum nanoparticles were deposited onto the carbon support using the sodium borohydride method. Thermogravimetric analysis, X-ray diffraction, low temperature nitrogen sorption and high resolution transmission electron microscopy methods were used to characterize the structure of materials. The synthesized catalysts were used as cathodes in the polymer electrolyte membrane fuel cell (PEMFC) single cell measurements. The polarization and power density curves were used to evaluate the activity of the materials synthesized. The electrochemically active surface area has been obtained in order to estimate the contact surface areas of platinum and Nafion® electrolyte. The values of the electrolyte resistance, polarization resistance and the activation energy were calculated from electrochemical impedance spectroscopy data. The carbon support material synthesized at 750 °C was found to be the best for PEMFC cathode.

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1. Introduction

Proton exchange membrane fuel cell (PEMFC) is one of the most promising candidates as an environmentally clean power source in various applications. Due to relatively high efficiency, the possibility to use bio- and regenerative fuels (including hydrogen), low operating temperature and quick start-up time, PEMFC can be used as a power generation unit for automotive applications and residential co-generation systems [1–3]. PEMFC produces electric energy from the electrochemical reaction between hydrogen gas as a fuel and oxygen gas as an oxidant. However, high overpotential for oxygen electroreduction in the cathode decreases the efficiency of fuel cell and therefore novel materials are being sought for PEMFC application [4–7]. Improved cathode catalysts could have a huge positive impact on fuel cell efficiency. Platinum is the most common catalyst material used at/in PEMFC electrodes. Apart from Pt, some other precious metals with high stability have been investigated as alternatives to Pt in fuel cells [8,9]. Various alloys and Pt-free electrocatalysts have also been studied, but these

materials have not proved to be as stable and active as Pt-electrocatalyst [10–13].

The efficiency of a catalyst depends strongly on the selection of an appropriate support material. The demands for support material are suitable porosity for quick mass transport, high electrical conductivity and stability towards carbon oxidation/reduction process, known as carbon corrosion. Various catalyst support materials have been studied, but carbon materials are the most widely utilized supports due to suitable conductivity and porosity [1]. M. Uchida et al. [14,15] demonstrated that the properties of the carbon support have significant impact on the PEMFC performance and to achieve further improvement in the cathode performance the structure of the catalyst layer should be carefully optimized. The corrosion of carbon support for conventional cathode catalysts is a critical problem for PEMFC durability in automotive applications [16–18]. Different carbon supports [19–25] have been tested during long-term catalyst optimization studies [16–18,26–30]. Carbon materials can be synthesized using various methods like high temperature carbonization of carbon rich organic precursors, but also selective extraction of non-carbon elements from carbides can be used to prepare so-called carbide derived carbons (CDCs) [19,21–27,29]. CDCs are unique micro- and mesoporous materials in which pore size, shape, uniformity and other parameters can be controlled in a very exact manner [19,21–29]. It has been suggested that CDCs are viable fuel cell

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catalyst supports that are capable of realizing the full activity of Pt nanoparticles with superior corrosion stability [26–30]. CDCs with well-defined properties are excellent objects to study the impact of carbon catalyst support properties on the performance of a PEMFC single cell. The aim of this work was to study the suitability of Pt nanoclusters activated CDCs in fuel cell application and to compare the properties of these materials with commonly used commercial carbon support Vulcan XC72 based single cell characteristics.

2. Experimental

2.1. Synthesis of microporous-mesoporous carbon

Mo$_2$C powder (−325 mesh, 99.5%, Sigma-Aldrich), loaded into a quartz vessel in a tube furnace, was reacted with Cl$_2$ (99.999%, AGA) at a flow rate of 50 cm^3 min^{-1} at synthesis temperatures (T_{synt}): 600, 750, 800, 850, 900 and 1000 °C for 6 h [24]. The by-product MoCl$_5$ was removed by the flow of excess Cl$_2$. After chlorination the products (microporous-mesoporous C(Mo$_2$C) carbon) noted as C(Mo$_2$C)600 °C, C(Mo$_2$C)750 °C, C(Mo$_2$C)800 °C, C(Mo$_2$C)850 °C, C(Mo$_2$C)900 °C and C(Mo$_2$C)1000 °C, were additionally treated with H$_2$ for 2 h at 800 °C in order to remove residual chlorine, chlorides, and oxygen-containing functional groups. During the heating and cooling steps the reactor was flushed with a stream of Ar (99.9999%, AGA). Synthesis temperatures were selected to prepare materials with a wide variation of specific surface area (S_{BET}) and microporosity-mesoporosity characteristics [24,25]. About 1 g of each C(Mo$_2$C) material was prepared.

2.2. Preparation of Pt-nanoclusters activated Pt-C(Mo$_2$C) catalysts

The Pt-nanoparticles were deposited onto carbon support by sodium borohydride reduction method [31]. The required quantity of H$_2$PtCl$_6 \times$ 6H$_2$O (99.9%, Alfa Aesar) was dissolved in Milli-Q$^+$ water (18.2 MΩ cm at 25 °C) to prepare a solution with Pt-salt concentration of ∼1 mM. The prepared solution was stirred at room temperature (22 ± 1 °C) for 1 h. The pH of the solution was adjusted to ∼8 through drop-wise addition of 20 wt% solution of NaOH (99.99%, Sigma Aldrich). The required amount of carbon powder was added into the aqueous solution of H$_2$PtCl$_6$. Thereafter, the NaBH$_4$ (≥98.0%, Aldrich) aqueous solution was prepared by dissolving NaBH$_4$ in Milli-Q$^+$ water, which was then carefully added to the previously prepared suspension. The reaction mixture was stirred for 2 h and left to settle overnight. The catalysts (noted as Pt-C(Mo$_2$C)600 °C, Pt-C(Mo$_2$C)750 °C, Pt-C(Mo$_2$C)800 °C, Pt-C(Mo$_2$C)850 °C, Pt-C(Mo$_2$C)900 °C or Pt-C(Mo$_2$C)1000 °C) were filtered, rinsed thoroughly with Milli-Q$^+$ water and dried at 80 °C. The mass percent of Pt in the catalyst materials synthesized was ∼70 wt% (14 at%, i.e electrode loading was ∼0.7 mg$_{Pt}$ cm^{-2}). The batch size of the Pt-C(Mo$_2$C) materials prepared was about 0.4 g.

2.3. Methods of structural characterization

The content of Pt in the catalysts was estimated using thermogravimetric analysis (TGA) in the atmosphere consisting of 80 vol% N$_2$ and 20 vol% O$_2$ using NETZSCH STA449F3. The temperature was varied from 40 to 1000 °C with a heating rate of 5 °C/min and with gas flow rate 120 cm^3 min^{-1}. Weight of the samples in the Al$_2$O$_3$ pan was 7–9 mg.

The X-ray diffraction (XRD) patterns for the studied materials were collected with a Bruker D8 Advance diffractometer with Ni filtered Cu$K\alpha$ radiation (0.6 mm wide parallel beam, two 2.5° Soller slits and LynxEye line detector). The scanning step of 0.01° for 2θ was applied from 16° to 90° and the total counting time per step was 166 s.

The porosity of the powders was estimated using the low-temperature (−195.8 °C) nitrogen sorption method [32] (Micromeritics ASAP 2020). The non-local density functional theory and the slit shape pore model were used for the pore size distribution calculation. The specific surface area, S_{BET}, values were calculated using the Brunauer-Emmett-Teller multipoint theory [32] within the relative pressure (p/p_0) range from 0.05 to 0.2. The total volume of pores (near saturation pressure), V_{tot}, and the volume of micropores, V_{micro}, were calculated using the t-plot method with Harkins and Jura thicknesses between 0.5 and 0.9 nm [33].

The cross-sectional view of the catalyst layer was measured using Microtrac Semtrac system. The high-resolution scanning electron microscopy (HRSEM) data were obtained using Helios^{TM} Nanolab 600.

2.4. Preparation of the membrane electrode assembly

Catalyst ink was prepared by suspending the Pt-C(Mo$_2$C) powder in solution of isopropanol (Sigma-Aldrich, >99%), Nafion$^®$ dispersion (Aldrich) (to achieve 20-25 wt% content of Nafion$^®$ ionomer in the final catalyst layer) and Milli-Q$^+$ water. The mixture was sonicated for 30 min to prepare uniformly dispersed ink. The catalyst coated membrane method was used to prepare the membrane electrode assembly (MEA). Catalyst ink was applied onto the Nafion$^®$115 membrane using spray gun and dried in vacuum oven at 50 mbar and 80 °C. To avoid the inhomogeneity in the catalyst layer caused by swelling, the MEAs were pressed before and after every coating procedure at 6 MPa in 80 °C using isostatic laminator (Keko ILS-66).

The geometric surface area of the electrode was 5 cm^2. The electrocatalyst loading was ∼1.0 mg cm^{-2}, including ∼0.7 mg cm^{-2} Pt in the form of deposited nanoclusters.

The MEA was placed between the graphite plates with septrine gas flow channels. PTFE gaskets (0.25 mm) and ELAT 1400W gas diffusion layers were used for assembling the single cell, which was held together by eight 6 mm bolts with a torque of 5 N m.

2.5. Single cell tests

Electrochemical measurements were performed using a potentiostat/galvanostat (PGSTAT302N, Autolab) connected to a booster (BOOSTER20A, Autolab). H$_2$ and O$_2$ were fed to the anode and cathode at a flow rate of 200 ml min^{-1} and 100% humidification at temperatures 30, 40, 50, and 60 °C. Gas flow was regulated and humidified using MKS Type M100B mass-flow controllers and a dew point humidification system (Fuel Cell Technologies, Inc.)

Polarization and power density curves were measured in the galvanostatic mode. Data were collected with 0.2 A current intervals and each point was measured for 60 s. The electrochemical impedance spectroscopy (EIS) measurements were performed in galvanostatic (current density j = 0.4 A cm^{-2}) and potentsiostatic (cell potential ΔE = 0.55 V) modes at frequency range from 0.5 to 100 000 Hz with an applied AC amplitude of 0.02 A and 0.005 V. The electrochemical surface area (ECA) was estimated from the H$_2$ adsorption method based on the analysis of current peaks in cyclic voltammograms measured within the potential range from 0.04 to 1.05 V at scan rates from 20 to 500 mV s^{-1} at 30 °C. Humidified N$_2$ was fed to the cathode at 200 cm^3 min^{-1} and H$_2$ to the anode at 10 cm^3 min^{-1}.

3. Results and discussion

3.1. Analysis of the physical characteristics of the materials

The thermogravimetric curve of the Pt-C catalyst measured in the synthetic air (Fig. 1) has a typical shape [34,35]. The oxidation