



Enhanced stability of multilayer graphene-supported catalysts for polymer electrolyte membrane fuel cell cathodes



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HIGHLIGHTS

- MLG-composites were applied as highly durable catalyst support for PEMFC cathodes.
- Remarkable positive effect of MLG-composites in term of the platinum utilization was shown.
- They lead to more than 9 times higher power density in comparison to the commercial standard.
- High electrochemical stability of MLG-containing cathodes was demonstrated.
- They showed no degradation but even a 13% higher power output after the AAP tests.

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ABSTRACT

One of the biggest challenges in the field of polymer electrolyte membrane fuel cells (PEMFC) is to enhance the lifetime and the long-term stability of PEMFC electrodes, especially of cathodes, furthermore, to reduce their platinum loading, which could lead to a cost reduction for efficient PEMFCs. These demands could be achieved with a new catalyst support architecture consisting of a composite of carbon structures with significant different morphologies. A highly porous cathode catalyst support layer is prepared by addition of various carbon types (carbon black particles, multi-walled carbon nanotubes (MWCNT)) to multilayer graphene (MLG). The reported optimized cathodes shows extremely high durability and similar performance to commercial standard cathodes but with 89% lower Pt loading. The accelerated aging protocol (AAP) on the membrane electrode assemblies (MEA) shows that the presence of MLG increases drastically the durability and the Pt-extended electrochemical surface area (ECSA). In fact, after the AAP slightly enhanced performance can be observed for the MLG-containing cathodes instead of a performance loss, which is typical for the commercial carbon-based cathodes. Furthermore, the presence of MLG drastically decreases the ECSA loss rate. The MLG-containing cathodes show up to 6.8 times higher mass-normalized Pt-extended ECSA compared to the commercial standard systems.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFC) [1–6] are considered a possible alternative to the internal combustion engine in the transportation sector. Due to their high costs related mainly to the expensive noble metal catalysts like platinum and its alloys, further optimization is required to meet the demands of this market. To the main price-issues belong the used platinum amount,

the durability and the performance loss of the fuel cell electrodes. A further problem is the low catalyst utilization. This means that during the manufacturing process significant amount of the catalyst is not located at the three-phase-boundaries (TPB) where the fuel cell reactions take place, thus contributing to the cost but not to the performance.

The durability of the PEM fuel cells [1–6] depends strongly on their operating conditions, application, stack and system design, but the key factors with respect to their durability are the properties of the electrode materials (catalyst support, catalyst, ionomer, electrolyte and their interaction in the TPB formation) and their integration in the MEA. PEMFC cathodes are exposed to high

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potentials above 0.9 V vs. reversible hydrogen electrode (RHE) at an open circuit, start, stop or fuel starvation and cell reversal, reaching even 1.5–2 V vs. RHE. The start–stop cycles cause high interfacial potentials at the cathode, which lead to a strong corrosion of the carbon catalyst support.

Degradation mechanisms have been described for PEM fuel cells during their operation [7–12]. One of them is the dissolution of platinum, especially from the cathode, which could be the main reason for the particle growth [7,8] and the active surface loss of the platinum catalyst through the deposition or dissolution mechanism.

Platinum is an effective catalyst for carbon support corrosion, while carbon loss decreases the distance between Pt particles promoting the Pt agglomeration and Pt detachment from the support. This mechanism consists of three steps: (i) Pt dissolution from the cathode, (ii) Pt ion diffusion in the polymer membrane electrolyte and (iii) Pt deposition in a reducing atmosphere. The formation of Pt band is strongly related to the Pt concentration in the electrolyte: the reaction rate in each step is slower for lower concentrations. The key factor to decrease the Pt band is the reduced solubility of Pt ions in an electrolyte membrane [7].

In order to prevent strong performance losses and to avoid this degradation mechanism [13], some proper mitigation techniques and robust materials are needed. From the materials development point of view the use of a more corrosion stable carbon support would be an obvious approach to solving the reverse-current decay mechanism, as the electrochemical oxidation of carbon results in performance decay. One of the commonly used techniques to improve stability is graphitization via heat treatment of carbon above 2000 °C, but the disadvantage of this technique is that it lowers the specific surface area and leads to a limited ability of adequate platinum dispersion. The carbon supports should possess surface area higher than 100 m² g⁻¹ to meet requirements for mobile applications [13,14].

The use of novel carbon supports like carbon nanotubes has already shown some success, but they are still in the stage of development. Another approach is the development of catalyst systems to minimize the strong electrochemical oxidation of carbon. This can be performed by addition of catalysts [15], which are corrosion stable in acidic environment and high anodic potentials, and are active for the oxygen evolution reaction (OER) like iridium oxides.

The most commonly used catalyst support material for PEMFCs is carbon black (Vulcan XC72™, BLACK PEARLS 2000™, Ketjen Black™, TIMREXTM HSAG400™, Ensaco 350G™, etc.). To optimize the known problems of the standard catalyst supports (rapid degradation, corrosion, agglomeration and dissolution of the supportive material and of the catalyst particles), different new materials like HGS (hollow graphitic spheres) [16], CNT (carbon nanotubes) [17–20], CNF (carbon nanofibers) [21,22], mesoporous carbon materials (pore size 2–50 nm) [23], OMC (ordered mesoporous carbons) [24,25], DOMC (disordered mesoporous carbons) [26], conductive diamonds [27], doped diamonds like BDD (boron-doped diamond) [28], carbonless materials like conductive oxides [29,30], or carbides [31] have been attempted.

MLG is a promising alternative to conventional carbon black materials which have lower electronic conductivity, lower specific surface area (e.g. Vulcan XC72™: 65 m² g⁻¹) and a lower level of graphitization. Another important aspect is the stability of the catalyst and support, which might be improved by the use of MLG. This can provide a more stable supportive material and strengthen the interaction of the catalyst with the support [32–34].

As shown previously [35], MLG-containing catalyst support layers show a formation of a very dense roof-tile structure, which is built during a coating process. This fact leads to a consequence that

a fuel cell MEA which contains this material as catalyst support exhibits mass-transport problems and a poor performance. For this reason it is necessary to add spherical or tube-like carbon spacers (different carbon blacks or MWCNT) which prevent the formation of a roof tile structure. Such a composite leads to a very porous and percolated system, which enables a very good mass-transport of educts/products and an enhanced electronic conductivity [35].

In this paper we demonstrate the immobilization of platinum catalysts on the surface of pure MLG and MLG/carbon black or MLG/MWCNT mixtures by a thermally induced chemical reduction method of a platinum precursor. This method has the advantage of decreasing the degree of agglomeration of platinum precursors during its reduction process due to their strong adsorption on the carbon surface. The catalyst loading can be controlled by the addition of the calculated amount of hexachloroplatinic acid. Thus produced samples were physicochemically characterized by transmission- and scanning electron microscopy (TEM, SEM), inductively coupled plasma optical emission spectroscopy (ICP-OES). The cathodes were used to prepare MEAs which were characterized in 50 cm² single fuel cells (in-house standard ZBT, water heated-version) by means of potentiodynamic, cyclic voltammetry, AC impedance and hydrogen crossover measurements during an AAP. We demonstrate the preparation of an efficient and durable Pt/carbon support system with the following properties:

- Enhanced electronic conductivity due to strong percolation of MLG.
- Improved electrochemical- and chemical stability at fuel cell operation temperatures between 60 and 100 °C.
- High specific surface area (70–200 m² g⁻¹), which improves the dispersion of the catalytic metals.

MEAs prepared with a MLG-based catalyst support system show longer lifetime by suppressing the catalyst degradation mechanisms. The use of a MLG-based catalyst support could reduce the production costs and improve the efficiency of fuel cell systems by (i) reducing the platinum loading by increasing the Pt utilization due to MLG's higher extended surface area and (ii) improving the lifetime of the fuel cell electrodes by reducing or stopping the degradation of the catalysts and supportive materials [35].

2. Experimental

2.1. Materials

Commercial MLG (AO-2) purchased from Graphene Supermarket (Calverton, New York) were used for the present studies. AO-2 has following properties: BET surface: 130 m² g⁻¹, average flake thickness: 30–40 monolayers (~10 nm) and average flake diameter: 5.3–8.0 μm.

2.2. Microscopic techniques

TEM pictures were taken with a JSM 6400 F instrument (Jeol, Munich, Germany). Samples were suspended with ethanol and applied on a TEM grid. SEM pictures were taken using a Jeol JXA-840A microscope and Helios NanoLab™ 600 (FEI, Eindhoven, Netherlands). The samples were fixed in the dry, powdery state on the sample holders (d = 2.5 mm).

2.3. Chemical characterization

Chemical impurities were determined by ICP-OES measured with a Varian 720-ES (Varian Inc., Palo Alto, California). The samples were weighed in the first step and reduced to ashes during a

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