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Oxidative Treatment to Improve Coating and Electrochemical Stability of Carbon Fiber Paper with Niobium Doped Titanium Dioxide Sols for Potential Applications in Fuel Cells

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ABSTRACT

Regular hydrophobized carbon paper cannot be used for unitized regenerative fuel cell applications as it corrodes at high potentials on the oxygen electrode side. Reported here are the oxidative treatment and dip-coating of carbon paper (Spectracarb™ 2050A-0850) with Nb-doped TiO_2 sols (anatase phase) to increase the corrosion resistance of the carbon paper at the interface between catalyst layer and gas diffusion backing layer. Coating of carbon paper with Nb-doped TiO_2 sols generates a reasonably uniform layer of TiO_2 and covers the individual carbon fibers well only if the carbon paper is oxidatively functionalized prior to coating. This can be reasoned with a better wetting of the functionalized carbon paper by the sol-gel and the formation of covalent bonds between Ti and the large number of functional groups on the surface of oxidized carbon paper, which is in good agreement with previous observation for carbon nanotubes. The resistance towards oxidation of coated and uncoated samples of untreated and functionalized carbon paper was probed by cyclic voltammetry in 0.5 M aqueous H_2SO_4 at 1.2 V versus Ag/AgCl for up to 72 hours to mimic the conditions in a unitized regenerative fuel cell. Among these four cases studied here, functionalized carbon paper coated with a layer of Nb-doped TiO_2 shows the highest stability towards electrochemical oxidation while uncoated functionalized carbon paper is the least stable due to the large number of available oxidation sites. These results clearly demonstrate that a coating of carbon fibers with TiO_2 generates a lasting protection against oxidation under conditions encountered at the oxygen electrode side of unitized regenerative fuel cells.

1. Introduction

Direct conversion of chemical energy into electrical energy in fuel cells has been broadly developed over several decades because it promises a clean and reliable alternative to combustion engines. The unitized regenerative fuel cell (URFC) is a rather recent technology among the many different kinds of fuel cells, which includes electrolyser and fuel cell in one unit [1]. Its further development is presently limited by the low stability of the bifunctional oxygen electrode for both reduction of oxygen and oxidation of water [2]. Particularly problematic is the commonly used hydrophobized carbon paper (or cloth) as gas diffusion backing (GDB) layer because it quickly corrodes at the high potentials of the oxygen electrode in URFCs [1].

The replacement of carbon paper by more corrosion resistant materials such as titanium fibers [3] and foams [4] has been demonstrated but they cannot compete with the weight and cost advantages of carbon paper. Commercially more promising appears to be the chemical modification of carbon papers. Song et al. [5] and Huang et al. [6] reported a high performance URFC based on a novel bifunctional oxygen electrode that consists of a corrosion-resistant carbon-based gas diffusion layer. They showed that highly active catalysts, such as IrO_2, react with the intermediate free radical oxygen species to less reactive oxygen molecules before they can reach the carbon based GDB layer. IrO_2 and similar coatings of iridium titanium nitride [6] and titanium carbide [7] were spray coated as powders to generate microporous layers on top of carbon paper. Consequently, the interface between the catalyst layer and GDB layer is still prone to corrosion and requires protection of the carbon material.

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A possible alternative approach is the direct coating of carbon paper fibers with a corrosion resistant metal oxide layer but this has not been attempted, to the best of our knowledge, and may be challenging due to the hydrophobic nature of the carbon surface and incomplete coating of all carbon fibers. Commercially most promising is the coating with titanium dioxide because of its low cost, low toxicity, high resistance to chemical and photo induced corrosion, and high thermal stability. TiO_2 is widely used not only as white pigment but also as semiconductor in, for example, photovoltaic [8], catalysis [9], and biomedical applications [10]. Most interesting as semiconductor is the anatase phase of TiO_2 with a band gap of 3.2 eV [11]. Its electronic conductivity can be increased by the introduction of appropriate dopants, such as Nb^{+5} [12]. Doping with Nb has also been shown to thermally stabilize the anatase phase and impede grain growth [13]. In fact, highly stable Pt/Nb-doped TiO_2 catalysts have been applied in PEM fuel cells [14,15]

Our focus is on TiO_2/carbon hybrid materials that combine the advantages of both titanium dioxide and carbon paper [16,17]. The most cost effective deposition of TiO_2 on carbon paper is deposition from solution, when compared to sputtering [18] and evaporation [19] techniques, but the lack of compatibility between the polar deposition solution and the rather inert and non-polar surface of the carbon paper remains a challenge [20,21]. Presented here is an oxidative pretreatment of the surface of carbon paper that generates polar groups (e.g. OH, C=O, and COOH) for direct dip coating with Nb-doped TiO_2 sols. This appears to be the first report on the oxidative modification of carbon papers/clothes/felts for a better coating with sol-gels, to the best of our knowledge, but has been widely applied in the functionalization of carbon nanotubes [20,22]. The presented coating methodology is versatile and not limited to the fabrication of corrosion resistant GDB layers for unitized regenerative fuel cells.

2. Experimentals

Fig. 1 shows the schematic representation of the procedure for oxidative functionalization of carbon paper and its coating with Nb-doped TiO_2. This scheme will be explained in sections 2.1 and 2.2. Then physical and electrochemical characterization techniques will be explained in sections 2.3 and 2.4, respectively.

2.1. Preparation of functionalized carbon paper

The surface oxidation of porous carbon paper (Spectracarb™ 2050A-0850 Engineering Fibers Tech. Shelton, CT) was achieved by applying a method previously reported for the oxidation of other carbon materials [23]. Three pieces of carbon fiber papers (15 mm × 15 mm) were thoroughly washed with acetone, dried, and submerged in 50 mL of concentrated sulfuric acid. $NaNO_3$ (5 g) was added to the sulfuric acid and stirred for an hour before the mixture was cooled down to 0 °C in an ice bath and 7.3 g of $KMnO_4$ were added in small portions over a period of 2 hours. When the addition was completed the temperature of the stirred mixture was increased to 35 °C for another 2 hours. Finally, the oxidation was completed by the addition of 200 mL of ice water and 7 mL of H_2O_2 (30%). The oxidized carbon paper was thoroughly washed with aqueous HCl (3%) followed by deionized water and dried in a vacuum oven at 50 °C for 24 hours. In the following the untreated carbon paper is denoted as UCP and the oxidatively functionalized carbon paper as FCP.

2.2. Preparation of $Nb_{0.1}Ti_{0.9}O_2$ coating on carbon paper

Nb-doped TiO_2 thin films on carbon paper were prepared by dip coating of the carbon paper into a stabilized Nb-doped TiO_2 sol gel [24,25]. Acetylacetone was used as stabilizing agent to prevent the rapid hydrolysis of alkoxide precursors with water. Titanium tetraisopropoxide (8 mL, 27 mmol) and niobium ethoxide (680 μL, 2.7 mmol) (calculated ratio for a final composition of $Nb_{0.1}Ti_{0.9}O_2$) were added to a vigorously stirred solution of 1.25 mL of acetylacetone in 50 mL of anhydrous ethanol under N_2 atmosphere. The solution was stirred for 2 hours and then acidified to a pH of about 3 by the addition of 8.5 mL of concentrated HCl. Stirring was continued with the solution being open to the environment until 70%

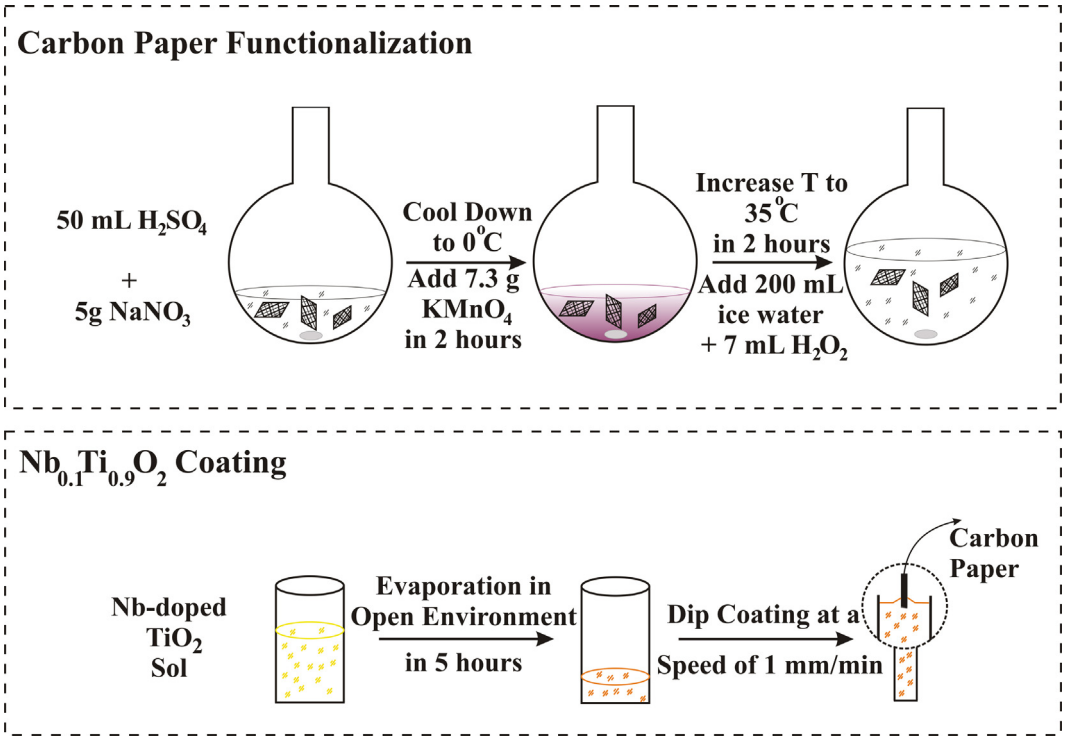

Fig. 1. Schematic representation of the procedure for oxidative functionalization of carbon paper and its coating with Nb-doped TiO_2.