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 TiO₂ 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 TiO₂ sols generates a reasonably uniform layer of TiO₂ 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 H₂SO₄ 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 TiO₂ 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 TiO₂ generates a lasting protection against oxidation under conditions encountered at the oxygen electrode side of unitized regenerative fuel cells.

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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. TiO₂ 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 TiO₂ with a band gap of 3.2 eV [11]. Its electronic conductivity can be increased by the introduction of appropriate dopants, such as Nb⁵⁺ [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 TiO₂ catalysts have been applied in PEM fuel cells [14,15].

Our focus is on TiO₂/carbon hybrid materials that combine the advantages of both titanium dioxide and carbon paper [16,17]. The most cost effective deposition of TiO₂ 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 TiO₂ 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. Experiments

Fig. 1 shows the schematic representation of the procedure for oxidative functionalization of carbon paper and its coating with Nb-doped TiO₂. 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. NaNO₃ (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 KMnO₄ 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 H₂O₂ (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 Nb₀.₁Ti₀.₉O₂ coating on carbon paper

Nb-doped TiO₂ thin films on carbon paper were prepared by dip coating of the carbon paper into a stabilized Nb-doped TiO₂ 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 Nb₀.₁Ti₀.₉O₂) were added to a vigorously stirred solution of 1.25 mL of acetylacetone in 50 mL of anhydrous ethanol under N₂ 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%