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Single-walled carbon nanotube buckypapers as electrocatalyst supports for methanol oxidation

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HIGHLIGHTS

- Different single-walled carbon nanotubes buckypapers have been obtained.
- PtRu nanoparticles between 2 and 15 nm were electrodeposited on SWCNT buckypapers.
- PtRu catalyst on SWCNTs from CoMoCAT process has high methanol oxidation activity.
- Solvent used for buckypapers preparation strongly influences catalyst dispersion.

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ABSTRACT

This work studies the use of various single-walled carbon nanotube (SWCNT) buckypapers as catalyst supports for methanol electro-oxidation in acid media. Buckypapers were obtained by vacuum filtration from pristine and oxidized SWCNT suspensions in different liquid media. Pt–Ru catalysts supported on the buckypapers were prepared by multiple potentiostatic pulses using a diluted solution of Pt and Ru salts (2 mM H_2PtCl_6 + 2 mM $RuCl_3$) in acid media. The resulting materials were characterized via SEM, TEM, EDX and ICP-OES analysis. Well dispersed rounded nanoparticles between 2 and 15 nm were successfully electrodeposited on the SWCNT buckypapers. The ruthenium content in the bimetallic deposits was between 32 and 48 at. %, while the specific surface areas of the catalysts were in the range of 72–113 $m^2\ g^{-1}$. It was found that the solvent used to prepare the SWCNT buckypaper films has a strong influence on the catalyst dispersion, particle size and metal loading. Cyclic voltammetry and chronoamperometry experiments point out that the most active electrodes for methanol electro-oxidation were prepared with the buckypaper supports that were obtained from SWCNT dispersions in N-methyl-pyrrolidone.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) are very attractive materials due to their exceptional geometry and properties at the nanoscale. SWCNTs exhibit excellent electronic conductivity and superior mechanical performance, high surface area, high chemical stability and also fast electron-transfer kinetics for electrochemical reactions. The preparation of SWCNT-based films has been up to date the most successful way to transfer SWCNT properties from the nano- to the microscale level [1], leading to formation of strong and light-weight materials [2]. As a result, SWCNT films are promising materials for flexible electronics, chemical and biological sensors, transparent electrodes in solar cells and displays, artificial actuators and nanostructured electrodes in batteries, supercapacitors and fuel cells [3].

Proton exchange membrane fuel cells (PEMFCs) are amongst the most promising alternative energy source for the near future, primarily to power electric vehicles and portable electronic devices. Nowadays, the most important goal of the researchers is to reduce the cost and to improve durability. The main strategy involves decreasing the platinum loading in fuel cell electrodes by optimization of the electrode structures and implementation of more active Pt alloy catalysts, as well as the development of highly-conductive membranes, although further work is required to optimize the combined performance and durability of catalysts and membranes in the membrane electrode assembly (MEA) [4].

Carbon nanotube buckypapers (BPs) are black paper-like sheets made of interwoven mats of nanotubes. BPs are extremely

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promising supports for platinum-based catalysts, because catalyst nanoparticles can be located on the most accessible external surface of the buckypaper network, improving Pt utilization. Besides, the empty spaces between the bundles of nanotubes can be filled by Nafion ionomer which facilitates the increase in the three-phase boundary [5]. Additionally, reactant access and product removal can be enhanced by modulating the inter-tubes porosity, either through the filtration pressure or the nanotubes concentration [6].

Several methods for synthesizing Pt nanoparticles on carbon nanotubes have been proposed [7]. Among them, electrodeposition is particularly attractive because it is a simple low cost method and also the metal particles can be deposited selectively at desired locations on the three-phase boundary with enough electron, proton and reactant access. There are some works dealing with the preparation of supported platinum catalysts over nanotubes films by electrochemical techniques [5,8–11]. Zhu et al. have published a series of reports focused to evaluate the behavior of carbon nanotube buckypaper films as catalyst supports for PEMFC [5,8–10]. The authors prepared catalysts with low and ultralow platinum loadings by electrodeposition, resulting in electrodes with a relatively high metal utilization, high activity and good durability in a single fuel cell test due to the maximization of the three-phase boundary. Ramesh et al. [11] evaluated the performance of Pt/BP electrodes with ultralow metal loadings as the cathode catalyst layer in PEMFC. They found that this electrode configuration improves the mass transport within the catalyst layer and increases the mass activity as well as produces an efficient proton transport without additional Nafion in the catalyst layer.

This work studies the use of various BPs as Pt–Ru catalyst supports. The influence of the buckypaper preparation on the characteristics of the electrodeposited catalysts and their activity for methanol oxidation is examined by SEM, TEM, EDX and electrochemical techniques.

2. Experimental

SWCNTs were purchased from Carbon Solutions Inc., Riverside, CA, USA (AP-SWNT grade) and from Sigma–Aldrich (704121). SWCNTs from Carbon Solutions (CS-SWCNTs) are synthesized by the electric arc reactor method using Ni/Y catalyst and contain ~30 wt. % metal residue. The average diameter and length of the CS-SWCNTs is 1.89 nm and 509 nm, according to atomic force microscopy measurements [12]. Sigma–Aldrich 704121 SWCNTs are supplied by Southwest Nanotechnologies, Norman, OK, USA (SWeNT SG 76 grade). These nanotubes (SW-SWCNTs) are synthesized by a chemical vapor deposition method utilizing cobalt and molybdenum as the catalysts (CoMoCAT process). According to the provider, SW-SWCNTs have diameters of 0.7–1.1 nm and an average length of 800 nm. Metal residue is less than 10 wt. %. More than 50% of the nanotubes show (7,6) chirality.

Six carbon nanotube buckypapers (BP1, BP2, BP3, BP4, BP5 and BP6) were prepared by vacuum filtration through 0.1 μm Omnipore membranes (Millipore). BP1, BP2 and BP3 were made of pristine CS-SWCNTs, while BP4 and BP5 contained oxidized nanotubes (Ox-CS-SWCNTs). Oxidation of the CS-SWCNTs was performed by thermal treatment in air atmosphere in an oven at 350 °C for 1 h. The weight change during the process was from 70 to 64 mg (8.6% weight loss). BP6 was made of pristine SW-SWCNTs.

For BP1, 30 mg of the CS-SWCNT powder was tip sonicated (UP 400S Hielscher, 0.5 cycles, 60% amplitude) in 25 ml of dimethylformamide (DMF), filtered and washed with ether. BP2 was prepared from a dispersion of the CS-SWCNT powder in aqueous 1% sodium dodecylbenzenesulfonate (SDBS). 60 mg of SWCNTs were mixed with 25 ml of the SDBS solution, bath sonicated for 30 min, tip sonicated for 1 h and magnetically stirred at 60 °C for 24 h. The resulting dispersion was centrifuged at 13,000 rpm (20,000 g) for 30 min and the supernatant was carefully decanted and filtered. BP3 was prepared from a poly-vinylidene-fluoride (PVDF) solution in DMF containing 5 mg of PVDF powder (Aldrich, $M_w \sim 534{,}000$) and 25 ml of DMF. A total of 30 mg of CS-SWCNTs were added to the PVDF/DMF solution and were twice bath sonicated for 30 min and tip sonicated for 1 h. For BP4 and BP5, 30 mg of Ox-CS-SWCNTs were tip sonicated in 25 ml of DMF and N-methyl-pyrrolidone (NMP), respectively. For BP6, 30 mg of SW-SWCNTs were tip sonicated in 25 ml of NMP. Curiously, BP6 experienced radial shrinkage after filtration, during the drying of the residual NMP.

Characterization of the SWCNT powder samples was performed by visible/near infrared (Vis/NIR) absorption spectroscopy and thermogravimetric analysis (TGA). Vis/NIR spectra were measured in 2 ml quartz cubettes utilizing a Bruker VERTEX 70 spectrometer (NIR region) and a Shimadzu UV-2401 PC spectrometer (visible region). The SWCNT powders were tip sonicated in aqueous 1% SDBS and diluted with the surfactant until adjusting the absorbance at approximately 0.4 units at 850 nm. TGA of the SWCNT powders was carried out in a Setaram balance, model Setsys Evolution, under an argon inert flow and a heating ramp of 5 °C min^{-1}.

Buckypapers sheets (~5 mg cm^{-2}) were stuck onto polished glassy carbon (GC) discs of 0.07 cm^2 exposed geometric area by using a Nafion solution (5 wt. %).

Conventional three-compartment glass cells were used to run the electrochemical experiments at room temperature with a PAR 263 potentiostat/galvanostat. The counter-electrode was a platinum wire, and a reversible hydrogen electrode (RHE) served as reference electrode. All potentials mentioned in this work are referred to this electrode. An inert nitrogen atmosphere was maintained over the electrolyte during the experiments.

The bimetallic catalysts were synthesized by electrodeposition at room temperature using freshly prepared diluted solutions of 2 mM H_2PtCl_6 + 2 mM $RuCl_3$ in 0.5 M H_2SO_4. The electrodeposition was carried out using multiple successive potentiostatic pulses ($E_1 = 0.05$ V, $t_1 = 5$ s; $E_2 = 0.5$ V, $t_2 = 5$ s), applying 90 consecutive cycles. After deposition, the electrodes were thoroughly rinsed with ultrapure water and tested in sulfuric acid solution using cyclic voltammetry (CV) at a sweep rate of 50 mV s^{-1}.

The active surface area of the electrocatalysts was determined by copper underpotential deposition (Cu-UPD). Experimental details have been described elsewhere [13].

The electrode performance for methanol electro-oxidation was measured in 1 M CH_3OH/0.5 M H_2SO_4 solution by applying a potential sweep at a scan rate of 50 mV s^{-1}. Chronoamperograms were obtained applying potential pulses for 15 min from an initial potential of 0 V. Current densities for methanol oxidation were normalized per milligram of Pt.

The morphology of the catalyst surface and the particle size were analyzed using TEM microscopy (JEOL JEM-2010). Bulk composition analysis was performed by an energy dispersive spectroscopy (EDX, Bruker XFlash 3001) probe attached to an SEM microscope (Hitachi S3000N).

The amount of Pt and Ru deposited on the substrates was estimated using ICP-OES analysis (Perkin Elmer 7300 DV).

3. Results and discussion

3.1. Characterization of the SWCNTs

Important details regarding the electronic character, diameter and chirality of the SWCNTs can be extracted from Vis/NIR absorption spectra (Fig. 1). CS-SWCNT spectrum shows the characteristic bands of metallic (M_{11} band) and semiconducting (S_{22} band) SWCNTs at approximately 600–800 nm and 900–1200 nm,