Journal of Energy Chemistry 25 (2016) 265–271

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

http://www.journals.elsevier.com/
journal-of-energy-chemistry/

Carbon nanotubes as conducting support for potential Mn-oxide electrocatalysts: Influences of pre-treatment procedures

Saskia Buller[a,*], Marius Heise-Podleska[a], Norbert Pfänder[a], Marc Willinger[a,b], Robert Schlögl[a,b]

[a] *Max Planck Institute for Chemical Energy Conversion, Stiftstraße 34-36, 45470 Mülheim an der Ruhr, Germany*
[b] *Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany*

ARTICLE INFO

Article history:
Received 9 December 2015
Revised 6 January 2016
Accepted 7 January 2016
Available online 30 January 2016

Keywords:
Multi-walled carbon nanotubes (MWCNT)
Surface modification
Raman spectroscopy
Manganese deposition
Zeta potential

ABSTRACT

Different oxygen and nitrogen containing functional groups were created on the surface of the multi-walled carbon nanotubes. The multi-walled carbon nanotubes were treated in ultrasonic bath with sulfuric or nitric acid. Furthermore the surface texture was modified by increase of the roughness. In particular after treatment with the oxidizing nitric acid, in comparison to the H_2SO_4 or ultra-sonic treated samples, craters and edges are dominating the surface structures. Manganese oxide was deposited on the multi-walled carbon nanotubes by precipitation mechanism. Various manganese oxides are formed during the deposition process. The samples were characterized by elemental analysis, microscopy, thermal analysis, Raman spectroscopy, and by the zeta potential as well as X-ray diffraction measurements. It was shown that the deposited manganese oxides are stabilized rather by surface texture of the multi-walled carbon nanotubes than by created functional groups.

1. Introduction

The energy challenge is a major project for today's society. Storage of energy can be fulfilled by the conversion of electricity into chemical energy carriers like hydrogen. The electrolysis of water requires catalytic active and stable electrode materials, which are currently platinum, iridium oxide or ruthenium oxides [1,2]. For global applications the expensive noble rare metals have to be replaced by alternative abundant materials like compounds of carbon and manganese oxides, which are promising candidates [3]. Stability while maintaining high activities of the materials is hereby a major challenge. Research with the focus on stabilization effects is required for a detailed understanding of corrosion during the electrolysis.

Carbon nanotubes (CNT) contain several interesting properties making these materials suitable for many applications. Due to their high specific surface area of about 250 m^2/g their utilization as support materials for organic molecules or inorganic particles for catalytic purposes is excellent [4,5]. Organic linkers can be attached to the surface of the CNT by a covalent bonding through various sidewall reactions as well via noncovalent Van-der-Waals interactions [6]. Adsorption of metal nanostructures is based on attractive Van-der-Waals and repulsive forces as described by the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory. Hereby the metal particles and the carbon surface are considered as capacitors. According to this concept of interactions between charged particles, it is obvious that a chemical treatment of the involved surfaces has a critical impact on the deposition effects. Particularly if one considers that only accessible active sites on the surface can contribute to the catalyst activity [7].

Multi-walled carbon nanotubes (MWCNT) are built of several cylinders, which are stacked into one another. Each cylinder consists of sp^2 hybridized carbon sheets, equivalent to rolled-up graphene. The connectivity of the ends of the graphene sheets defines the two possible orientations, namely armchair or zigzag, respectively. The electronic properties make CNT very versatile as conductive support materials for electrodes in electrocatalysis [3]. Surface functional groups as well as defects in the outer layer of the MWCNT dominantly affect its properties. Modifications of the surface can be performed by gaseous or liquid treatment [8–10]. The morphology of the samples treated in gas phase thereby remains nearly unaffected [11]. The modified material properties show an improved performance in catalytic applications [12] or provide anchoring groups for the deposition of metal particles [13]. Depending on the treatment method, different types of functional groups can be created. By liquid nitric acid treatment more

---

[*] Corresponding author. Tel: +49 208 3063701; Fax: +49 208 3063951.
E-mail address: saskia.buller@cec.mpg.de (S. Buller).

http://dx.doi.org/10.1016/j.jechem.2016.01.022

carboxylic, anhydride and hydroxyl groups are formed, while by gaseous phase (5% O_2 in N_2) treatment more carbonyl and quinone groups are formed [14].

Manganese oxides exist in various oxidation states, and within the states in different structures like α-, β-, δ-MnO_2, or as amorphous phase. They are studied as electrocatalysts for water splitting, as anode for oxygen evolution reaction (OER) and, furthermore, as cathode for oxygen reduction reaction (ORR) [15,16]. In comparison to commonly used noble metal-based catalysts like platinum, palladium, iridium oxides, or ruthenium oxides, manganese oxides are inexpensive, natural abundant and environmental friendly. It was reported that the total oxidation of ethyl acetate by a dynamic mechanism including Mn^{4+} and Mn^{3+} oxide occur, which leads to the conclusion that Mn-oxides are active in manipulating the oxygen molecule chemistry. Further, manganese oxides are also known to be active materials for capacitors [17,18]. An enhancement of the capacitance of pure graphene by a factor of three up to 310 F/g was reported, caused by manganese oxide deposition [19].

Both components, carbon and manganese oxides are interesting materials for electrocatalysis. The combined dual functions of charge carrier transport and redox activities of oxygen are the relevant properties here. In order to define a structure–function relation, a first understanding of the chemical interaction between the metal oxide and the MWCNT surface is needed. In this work, we study the influence of different treatment methods on MWCNT and their stabilization effects on deposited manganese oxides. Investigations were performed with increasing quantities of deposited manganese.

2. Experimental

2.1. Cleaning and pre-functionalization of MWCNT

MWCNT produced by Shandong Dazhan Nano Materials Co. were separated in three batches. For the reaction with nitric or sulfuric acid, in each case 20 g of MWCNT were mixed with 500 mL of acid, stirred and heated up under reflux at around 100 °C for 16 h (H_2SO_4) or 3 h (HNO_3). After the reaction the gaseous supernatant was purged with nitrogen to remove acidic vapor for better handling. The material was filtered and washed extensively in a washing cell over night with distilled water to remove residual acid and impurities like iron. The initial amount of iron was reduced by these acid treatments by around two third. The third batch counts as reference for pure MWCNT. Treatment in ultra-sonic bath for 2 h at room temperature was applied to remove amorphous carbon from the surface as described in literature [20].

2.2. Impregnation of MWCNT with manganese (II)

The pre-functionalized MWCNT were divided into portions of 1.9 g each, and then wetted with distilled water to fill the inner channels of the carbon nanotubes. This favors a deposition on the outer surface of the MWCNT, following the selective deposition described in literature [21]. To obtain different loadings of manganese on each portion of the MWCNT, 20 mL of manganese (II) nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$, Merck) solutions with increasing concentrations of 0.06 mol/L, 0.12 mol/L, and 0.18 mol/L, were added dropwise under stirring. For the loading of the ultra-sonic bath treated samples concentrations of 0.018 mol/L, 0.09 mol/L, and 0.18 mol/L were used. The pH value was kept constant at pH 8. The products were dried at 60 °C for 6 h and afterwards at 110 °C for 24 h in air.

2.3. Elemental analysis

The elemental analysis was executed by the external analysis laboratory Kolbe (Höhenweg 17, 45470 Mülheim an der Ruhr, Germany), using a Vario EL CHNOS-Analyzer from elementar company.

2.4. N_2 sorption measurements

N_2 sorption measurements were performed with an Autosorb6 (Quantachrome) at 77 K. The samples were outgassed for 2 h at 110 °C. The evaluation of the data was done by BET theory.

2.5. Microscopy

STEM Microscopy images were taken by a Cs corrected Hitachi HD-2700 STEM with a cold field emission gun and an accelerating voltage of 200 kV, equipped with an EDAX Octane T Ultra W EDX (energy dispersive X-ray) detector. HAADF and corresponding annular bright field STEM images were recorded using a double Cs corrected JEOL ARM microscope with a cold field emission gun. The instrument was operated at 200 kV.

2.6. Thermal analysis

Thermoanalytic analyses were performed with a NETSCH STA449F3 thermobalance setup connected to a quadrupole mass spectrometer (MS) QMS 403 D from Aëolus. Measurements were taken in Ar atmosphere with a constant gas flow of 50 mL/min in a temperature range of 40–1000 °C with a heating rate of 20 K/min. The corundum ceramic crucibles were filled with approximately 20 mg of sample material for the measurements.

2.7. Zeta potential

Zeta potentials were measured by a ZetaPALS90 analyzer from Brookhaven Instruments Corporation, equipped with an autotitrator. The principle of phase analysis light scattering (PALS) to determine the electrophoretic mobilities exhibits a 100 times higher precision than measurements by Doppler shift as described in detail in literature [22]. The phase shift was measured using a 639 nm laser, whereas the current of the cell was automatically adjusted at around 2 mA. 20 mL of the dissolved sample was dispersed in an ultra-sonic bath for 5 min and analyzed within a range of pH 10 to pH 2 adjusted by drops of NaOH and HNO_3.

2.8. Raman spectroscopy

Raman spectra were measured using a Thermo Scientific DXR Raman Microscope with a 50x magnification and a 532 nm laser. The samples were measured for 2 s and an exposure rate of 2 with a laser power of 3 mW. The fitting procedure is described in detail in literature [23]. Briefly, two defect peaks (D, D’) and one graphitic peak (G) were fitted to determine their percentage of the framework of the MWCNT. The D*/G ratio corresponds to the degree of defect sites calculated by the peak areas of the total sum of D- and D’-bands and the ideal graphitic band.

2.9. X-ray diffraction (XRD)

X-ray diffraction patterns were recorded in Bragg–Brentano geometry on a Bruker AXS D8 Advance theta/theta diffractometer, using Ni filtered Cu *Kα* radiation and a position sensitive LynxEye silicon strip detector.