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BRIEF COMMUNICATION

Synthesis of tungsten carbide nanopowder via submerged discharge method

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Abstract Tungsten carbide nanopowder was prepared via pulsed discharge of bulk tungsten and graphite rods immersed in pure ethanol. The effect of discharge parameters on the characteristics of final products was investigated. Structural and morphological characterization of nanopowder was performed by means of X-ray diffraction analysis and transmission electron microscopy. In order to determine the feasibility of using synthesized material as an electrocatalyst, tungsten carbide nanopowder was tested for hydrogen evolution. A correlation was found between morphology of nanoparticles, their phase composition and electrocatalytic activity.

Keywords Nanopowder · Submerged discharge · Hydrogen evolution reaction (HER) · Non-precious metal catalyst · Nanoparticle synthesis

Introduction

With the increasing need to develop alternative forms of energy, the search for the novel catalysts for hydrogen evolution is being intensified, as molecular hydrogen, H_2, is being considered as an energy carrier (Bockris et al. 1998; Appleby and Foulkes 1987). Currently, the most effective catalysts for hydrogen evolution process whereby protons and electrons are combined into molecular hydrogen are Pt group metals (Dresselhaus and Thomas 2001). However due to the high cost of these metals, a strong motivation exists to find inexpensive non-noble metal alternatives. Levy and Boudart demonstrated in 1973 that tungsten carbide displayed Pt-like behaviour in several catalytic reactions (Levy and Boudart 1973). Since that time many efforts have been devoted to evaluate the feasibility of using tungsten carbide and other tungsten-based materials as electrocatalyst (Yang and Wang 2005; Rosenbaum et al. 2006; Hwu and Chen 2003; Liu et al. 2003; Xu et al. 2007). Zheng et al. reported that nano-cristalline tungsten carbide thin film exhibited the catalytic activity for hydrogen evolution (Zheng et al. 2005).

The purpose of this paper is to describe a preliminary investigation of tungsten carbide

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nanopowder and its possibilities of use as catalytic materials for hydrogen evolution reaction (HER). The tungsten carbide nanoparticles were synthesized via submerged pulsed discharge method. This non-vacuum method has been reported recently to be the lowest cost method for synthesis of various nanostructures (Ishigami et al. 2000; Sano et al. 2001, Sano 2004; Sano and Ukita 2006; Bera et al. 2004; Bera et al. 2006; Parkansky et al. 2006; Muthakarn et al. 2006; Burakov et al. 2005). In this study we investigated the effect of discharge parameters on morphology of synthesized nanoparticles and their electrocatalytic behaviour towards HER.

Experimental

The experimental setup for nanopowder synthesis is schematically shown in Fig. 1. It consisted of four main components: a power supply system, the electrodes, a cell (glass beaker) and a chilling loop. A pulsed discharge was generated between two electrodes being immersed to a depth of 3 cm in 100 mL of ethanol (96%). The choice of ethanol was motivated by the fact that organic compounds play a role of a carbon source to produce nanoparticles in discharge-in-liquid system (Parkansky et al. 2006; Muthakarn et al. 2006). Tungsten and graphite rods with diameters of 6 mm were employed as electrodes, and the tips of the rod were sharpened. An optimum distance between the electrodes was kept constant at 0.3 mm to maintain a stable discharge. The discharge was initiated by applying a high-frequency voltage of 3.5 kV (power supply DG-1, USSR). The power supply system allowed to maintain several different types of pulsed discharge. One of them is the arc discharge and the second is a spark discharge. Both direct current (dc) and alternating current (ac) pulsed discharges were generated with repetition rates of 100 and 50 Hz respectively. The synthesis was carried out at an open circuit potential of 260 V and 220 V for dc and ac current discharges respectively. Current I(t) was recorded during the discharge as a function of time by means of an oscilloscope. The peak current of the arc discharge was 9 A with a pulse duration of 4 ms. The peak current of the pulsed spark discharge was 60 A with a pulse duration of 30 μs.

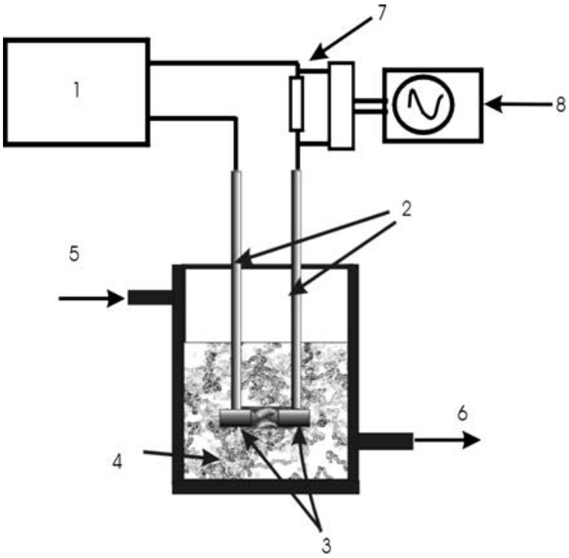

Fig. 1 Schematic diagram of the setup for nanopowder synthesis by submerged discharge method; (1) power supply; (2) electrodes holders; (3) electrodes; (4) liquid; cooled water (5) in and (6) out; (7) current sensor; (8) oscilloscope

Most of the synthesized products were obtained as suspended powder. After a presedimentation time (ca. 15 min), solid deposits sunk at the vessel bottom. To separate the suspended nanopowder from the sediment, discharge treated liquid was carefully poured in a Petri dish excepting last 10 mL with solid sediment. These suspended nanoparticles were characterized by transmission electron microscopy (TEM), X-ray diffraction analysis (XRD) and cyclovoltammetry (CV) for their size, morphology, crystalline structure and electrocatalytic activity for HER. A small quantity of liquid was removed from the Petri dish using a pipette and transferred to an amorphous carbon coated Cu grid used for TEM. Thereafter the liquid was allowed to evaporate at the temperature of 80 °C. The deposit obtained on the bottom of Petri dish was examined by XRD and CV. TEM was performed on a LEO 906E (LEO, UK, Germany) microscope operated at 120 kV. Powder composition and its crystalline structure were characterized by using X-ray diffraction at CuK_{α} (D8-Advance, Brüker, Germany). Standard-less semi quantitative phase analysis was performed with Diffrac Plus EVA in combination with PDF-2 database and Diffrac Plus TOPAZ. Electrochemical measurements were done with a model PG STAT 20 potentiostat/galvanostat from Eco Chemie (Utrecht, The Netherlands). For the electrochemical tests, tungsten carbide powder was deposited onto a graphite plate electrode with the geometrical surface area of 1 cm^2 using 5% Nafion solution as binder. The catalyst loading was 10 mg cm^{-2}. The nanopowder was investigated for HER in 1 M KCl solution (pH = 4.8) under N_2 purging. The scan rate was 5 mV s^{-1}. An Ag/AgCl was used as a reference electrode and Pt was used as counter electrode.

Results and discussion

Table 1 summarized the variation in synthesis rate and phase composition of nanopowders with the discharge parameters. As a general tendency, the synthesis rate was order of magnitude higher for spark discharge than that of arc discharge. It may be due to the difference in current value (Bera et al. 2006). For both arc and spark discharges, it was found that the synthesis rate was lower when tungsten was acting as a cathode. This result is consistent with literature data. Bera et al. reported that the consumption of anode is higher than that of cathode (Bera et al. 2004; Bera et al. 2006).

X-ray diffraction data were collected to characterize the samples. Figure 2 shows the typical XRD patterns, and Table 1 presents the results of semi-quantitative analysis of phase composition. As it can be seen, the synthesized nanopowder was a mixture of hexagonal W_2C (diffraction peaks at 2θ around 34.7°, 38.2°, 39.8°, 52.3°, 62.1°, 69.9°, and 75.0°), face centered cubic WC_{1-x} (diffraction peaks at 36.8°, 42.8°, 62.0°, 74.1°, and 78.1°) and hexagonal C (peak with 2θ value of 26.5°). Amorphous carbon is known to contribute to the broadening of XRD peaks in the ranges of $2\theta = 20° - 30°$ and $2\theta = 40° - 50°$ (Zellner and Chen 2005). It is worth noting that the diffraction patterns of samples showed no intensive diffuse peaks that can be attributed unambiguously to amorphous carbon. No peaks corresponding to W_xO_y were observed. Nanopowder contained also small amount body centered cubic W (diffraction peak at 40.3°, not shown in Fig. 2) when synthesis was performed via dc current spark discharge with tungsten rod acting as cathode. Here, the particular behaviour of this discharge should be stressed, showing rather high ability to synthesize W_2C. Moreover, in contrast to the other spark discharges, synthesized material contained relatively small amount of graphite. On the other hand, applying the tungsten as a cathode material appears to reduce C content in nanopowder prepared via arc discharge too. Generally, the content of C was higher and content of WC_{1-x} was lower when synthesis was performed by spark discharge.

Figure 3 shows the representative TEM images of (a) nanopowder synthesized by arc and (b) by spark discharges. Both images were taken at 1,00,000 times magnification. Nanoparticles prepared by arc discharge were observed in their agglomerated form. Because of agglomeration, it was difficult to measure correctly their size. However, as is evident from Fig. 3a, these agglomerations consisted of primary particles, typically 5–10 nm in size. The primary nanoparticles seemed to form three-dimensional (3D) structures. Small dark spots in Fig. 3a likely indicate this process. The agglomerated nanoparticles were surrounded by the arrowed grey regions, which were probably carbon layers, as shown in Fig. 3a. This typical view was seen everywhere in TEM images of product synthesized by arc, for both ac and dc current discharges irrespective of electrodes polarity. That fact implies that the morphology of synthesized nanopowders was governed rather by the current

Table 1 Summary of nanopowder synthesis conditions and results of nanopowder characterization by XRD

	Discharge type	Electrodes	Synthesis rate, mg/min	XRD-analysis			
				W_2C, vol. %	WC_{1-x}, vol. %	C, vol. %	W, vol. %
1	ac arc	W; C	0.2	7.1	78.1	14.7	–
2	dc arc	W(cathode); C(anode)	0.1	6.2	90.1	3.7	–
3	dc arc	W(anode); C(cathode)	0.2	6.6	71.5	21.9	–
4	ac spark	W; C	2.5	5.8	32.8	61.4	–
5	dc spark	W(cathode); C(anode)	1.2	57.0	30. 7	8.9	3.3
6	dc spark	W(anode); C(cathode)	2.1	5.6	32.5	61.8	–

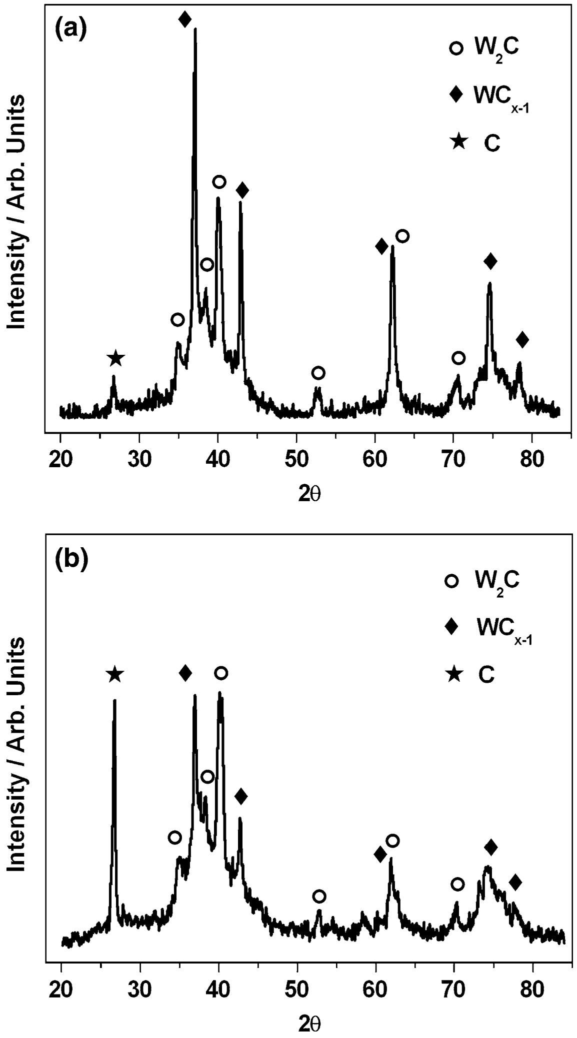

Fig. 2 XRD patterns of (**a**) nanopowder synthesized by ac arc discharge and (**b**) nanopowder synthesized by ac spark discharge

pulse duration and value of peak current than the polarity of the electrodes. Figure 3b demonstrates that the nanoparticles synthesized by spark were nearly spherical with a mean diameter of ~7 nm. The particle size distribution with standard deviation of 0.4 nm is shown in the inset picture of Fig. 3b. Comparison of morphology of nanoparticles from Fig. 3a and b implies that agglomeration may have occurred during discharge. Otherwise, the agglomerated nanoparticles would be observed in all experiments. The agglomeration process required low peak current (a few A) and long discharge duration (a few ms).

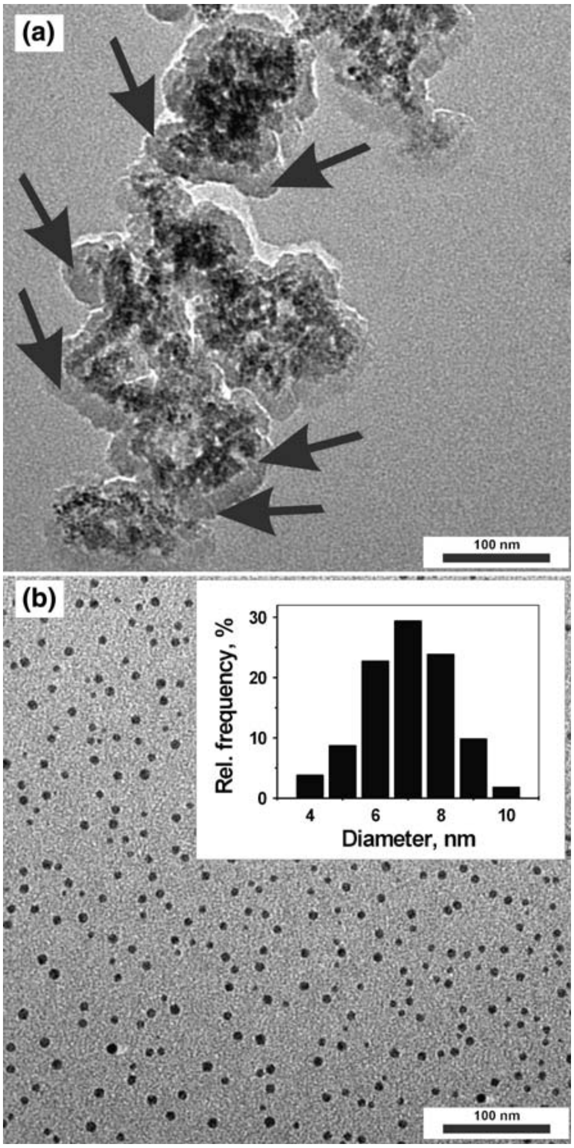

Fig. 3 TEM images of (**a**) nanopowder synthesized by ac arc discharge and (**b**) nanopowder synthesized by ac spark discharge. The nanoparticles size distribution is shown as an inset

Figure 4 displays CV curves for (a) nanopowder synthesized by arc discharge and (b) nanopowder synthesized by spark discharge. Cyclic voltammogram obtained on pure Pt is added as a reference. At the same potential, the absolute value of current was higher when using materials synthesized by arc discharge. It indicated that the catalytic activity of nanopowder prepared by arc was higher than that of nanopowder synthesized by spark discharge. For all

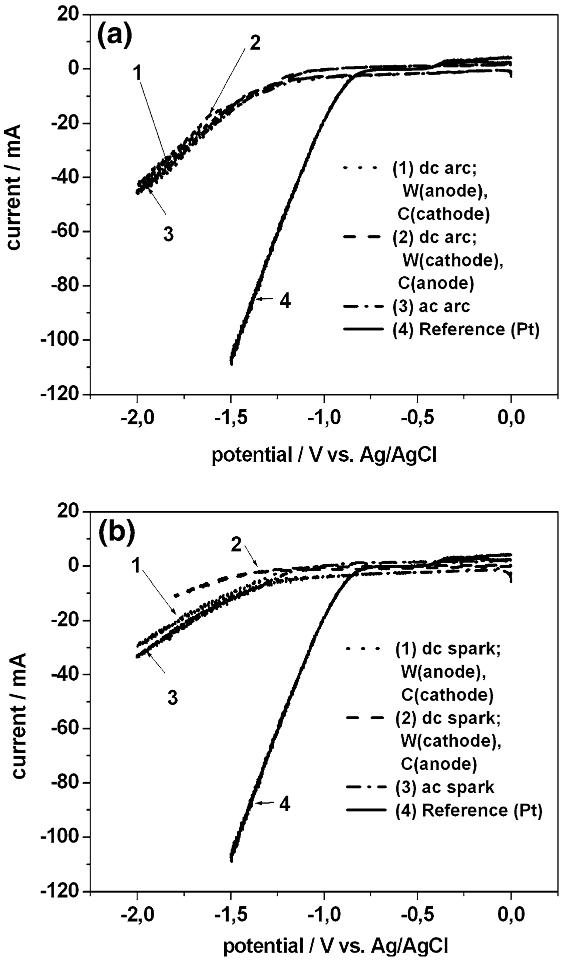

Fig. 4 Cyclic voltammograms on electrodes prepared with nanopowder synthesized by arc discharge (**a**) and nanopowder synthesized by spark discharge (**b**) in 1 M KCl electrolyte solution, pH 4.8, under nitrogen purging

three samples synthesized via ac and dc arc discharges, the CV curves were almost identical irrespective of the polarity of the electrodes in discharge (Fig. 4a). These samples having relatively low W_2C content and relatively high WC_{1-x} content may exhibit similar catalytic activity due to the similar composition (see Table 1). Whereas for samples prepared by spark method, there was a marked difference in electrocatalytic activity and composition. The nanopowder exhibited the least activity when it was produced by discharge with tungsten acting as a cathode (Fig. 4b). In contrast to the other samples, it contained high amount of W_2C (57 vol. %). On the other hand, the WC_{1-x} content was similar for all samples synthesized by spark discharge.

These results imply that the high content of W_2C in nanopowder may suppress its electrocatalytic activity for HER. An increase in WC_{1-x} content seemed to result in increasing electrocatalytic activity of nanopowder. In additional, generally higher activity of nanopowder prepared by arc discharge might be ascribed to its morphological features. It is believed that the enhanced stability and catalytic activity can be attributed to the protective properties of carbon layers and improved interface between the active sites and support (Kosugi et al. 2004; Moon et al. 2006; Zou et al. 2006; Manzoli and Boccuzzi 2005). These features of carbon shells may be at the origin of the enhanced activity of nanopowder synthesized by arc discharge. The nanoparticles surrounded by carbon layers may act as in-situ prepared supported catalyst having the better interface between the active species and support.

Conclusions

From the results and discussion presented above, the following conclusions can be made.

A pulsed discharge between two electrodes immersed in ethanol is a suitable method to produce nanoparticles with different contents of metal and carbon in a controllable way. By varying the current value and its pulse duration, morphology of nanoparticles and their composition can be changed. Synthesized nanoparticles can act as catalysts for HER. An increase in WC_{1-x} content in samples resulted in improvement of their catalytic performance. Among samples having similar WC_{1-x} content, it was observed that increasing of W_2C content led to reducing the catalytic activity. Agglomerated nanoparticles surrounded by carbon layers exhibited generally higher activity than that of well dispersed nanoparticles.

Work is continuing to further optimise tungsten carbide-based catalysts in order to improve their stability.

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