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RESEARCH ARTICLE

Synthesis and Electrochemical Performance of Tungsten Carbide

I. JOSHI, K. KHATI, A. BISHT, R. REKHARI, S. MEHTAB and M. G. H. ZAIDI

Department of Chemistry, G.B. Pant University of Agriculture and Technology, Pantnagar, Uttarakhand-263145, India

ilajoshi15@gmail.com

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Abstract: Tungsten carbide (WC) was synthesized *via* modified polymer precursor method. The formation of WC was ascertained through Fourier-transform infrared spectra (FT-IR), x-ray diffraction (XRD), thermogravimetry analysis (TGA) and differential thermo analysis (DTA). The WC electrode was synthesized over 316 stainless steel to evaluate electrochemical performance through cyclic voltammetry (CV). The CV curves of WC electrode were found in the potential span of -0.6 to 0.0V in KOH (1.0 M). The WC electrode shows specific capacitance (Cs) of 110 F/g at 0.001 V/s and good cyclic stability over 500 cycles.

Keywords: Tungsten carbide, Cyclic voltammetry, Electrochemical capacitance

Introduction

Supercapacitors (SCs) also known as electrochemical capacitors are energy storage devices having similarities with batteries and conventional capacitors but unlike batteries they store only electric energy[1]. SCs serve for bridging the energy gap between traditional capacitors with high power output and batteries with high energy storage capacity [2-4]. The charge storage capacity of SCs mainly depends on the type of electrode materials. The materials having high surface area, good electrical conductivity and thin electrolytic dielectrics are more reliable for energy storage devices[1]. Therefore, the new category of material *i.e*., metal carbides and nitrides recently have been introduced due to its exceptional chemical and physical characteristics[5].

The atoms like carbon, nitrogen and oxygen are easily dissolve in the interstitial sites of early transition metal lattice. Therefore, the resultant alloys are identified as metal carbides, nitrides and oxycarbides[6]. Due to their high strength and durability, they are used for making rocket nozzles and drill bits under utmost temperature and pressure[7]. Transition metal carbides are also widely used in the field of technology due to their high catalytic, magnetic and electronic properties[8-12].

In this paper, we investigate the electrochemical behavior of tungsten carbide (WC) electrodes for energy storage. We have also studied the charge-discharge characteristics of WC electrode.

Experimental

Ammonium metatungstate (AMT), resorcinol and formaldehyde were purchased from Sigma-Aldrich. Chlorosulfonic acid (98%) was procured from Across Chemicals, PSO (M_n, 26,000) from Aldrich Chemicals and graphite (500 µm) from Loba. Other chemicals and solvents were used without further purification.

Synthesis of WC and SPS

WC was synthesized using a modified polymer precursor route procedure[12]. Typically, 5.00 g of AMT and 1.25 g of resorcinol were dissolved in 1.65 mL of formaldehyde and 20 mL of de-ionized water. The resultant solution then refluxed at 90 ^{o}C for one day. Then precipitate of WC was washed with de-ionized water and dried at 50±1 °C/400 mm Hg over 24 hours.

PSO resin (7.2 g) was dissolved in dichloromethane (DCM) (75 mL) in a two neck flask at 20±1 ^{o}C under stirring at room temperature. To this the solution of chlorosulphonic acid in DCM was added drop wise with stirring over 2 h. The precipitated SPS was filtered and washed with NaOH (10%). Finally, SPS was washed with de-ionized water and dried at 50±1 °C overnight[13].

Preparation of the working electrodes

The metallic substrates for electrode (2 cm^2) area were fabricated through cutting a commercially available 316-SS sheet. Prior to deposition of electroactive material, surface of electrode was well polished with emery paper (mesh size 320600), followed by cleaning the surface with acetone. Working electrodes were prepared through depositing (100 µL) an ultrasonically prepared suspension comprising electroactive material (65 mg), graphite (10 mg) and SPS in NMP (5 g/dL) over SS substrate. The treated electrodes were dried at room temperature for 8 h, followed by 60 ºC/400 mm Hg for 48 h. This has afforded electrodes with a mass thickness of electroactive materials by 0.04±0.01 mg[13-14].

Characterization

FT-IR spectra of samples were recorded on thermo Nicolet in KBr from 4000 to 500 cm^{-1} on transmission mode. Thermo-oxidative stability was investigated through TG and DTA over EXSTAR TG/DTA 6300 instrument in static air at a heating rate of 10 ^{o}C/ minutes a flow rate of 200 mL/min in the temperature up to 700 ºC. XRD spectra of powdered samples were recorded at room temperature over Rigaku-Geigerflex, x-ray diffractometer using Cu-Kα radiation (λ= 0.154 nm) in the range of 5º-90º.

All the electrochemical characterizations were made over IVIUM Potentiostat-Galvanostat using a three electrode cell assembly. Ag/AgCl was used as reference electrode. Pt electrode was used as counter electrode. CV was conducted at current compliance 1 mA in the range of -0.6-0.0V, at 0.001-0.2 V/s at ambient temperature.

Results and Discussion

Spectra

FT-IR spectra

Figure 1, depicts the FT-IR spectra of WC. WC shows symmetric stretches near the low frequency fingerprint region at[15] 665.82 cm^{-1}. The peak at 3583.31 cm^{-1} corresponds to symmetrical stretch of W…..OH, probably due to moisture[16,17].

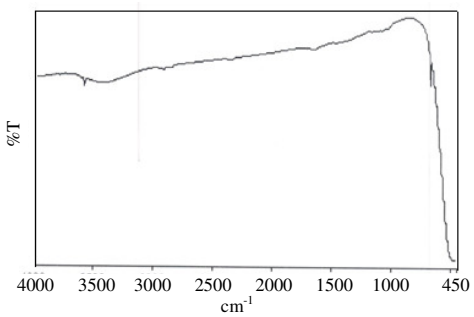

Figure 1. FT-IR spectra of WC

XRD spectra

The XRD spectra of WC are shown in Figure 2. For WC, the diffraction peaks at 31.49° (2.83), 35.70° (2.51), 48.35°(1.88), 64.16° (1.45), 65.70°(1.41), 73.22°(1.29), 75.67°(1.25), 77.12°(1.23) and 84.20°(1.14) are correspond to [001],[100], [101], [110], [002], [111], [200], [102] and [201] planes of hexagonal WC and well matched with JCPDS 73-0471[18].

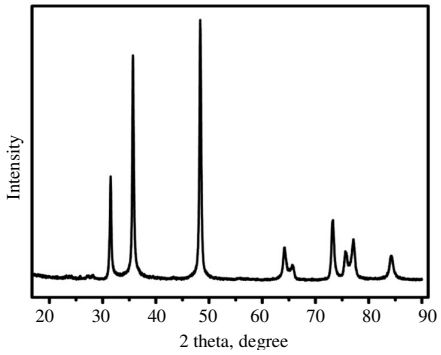

Figure 2. XRD spectra of WC

Thermal stability

Figure 3, display the TG and DTA of WC. WC was thermally stable up to 384 °C. WC was decomposed with TG onset at 528 °C. This was accompanied with weight gain of 4.90% due to oxidation[18]. Decomposition of WC was supported with a DTA signal (0.22 mV) at 548 °C. Maximum decomposition of WC was @ -21.97X10^3 mg/ °C at 552 °C. The TG endset of WC was appeared at 597 °C leaving char residue of 114.70 wt %.

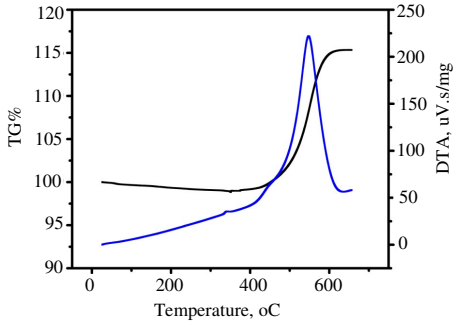

Figure 3. TG-DTA of WC

Electrochemical behavior

The electrochemical behavior of WC were examined through CV using KOH (1.0 M) as an electrolyte at the common scan rate of 0.001 to 0.2 V/s (Figure 4). A regular increase in the peak currents has been observed on increasing scan rate in the potential range of -0.6 to 0.0 V *vs.* Ag/AgCl. Calculations based on cathodic and anodic current reveals that WC display Cs (F/g) of 110.00 @ 0.001V/s (Figure 4a, 4b). Further to investigate, the cyclic performance of WC, the scans was run upto 500 cycles at a scan rate of 0.1 V/s. The electrode shows good cyclic stability with negligible loss of Cs (Figure 4c). The charging-discharging curve of WC electrode was recorded in the voltage range from -0.6 to 0.0 V at an applied current density of 10 mA/cm^2. The charge-discharge curves are linear in the full potential span, depict good capacitive behavior (Figure 4d).

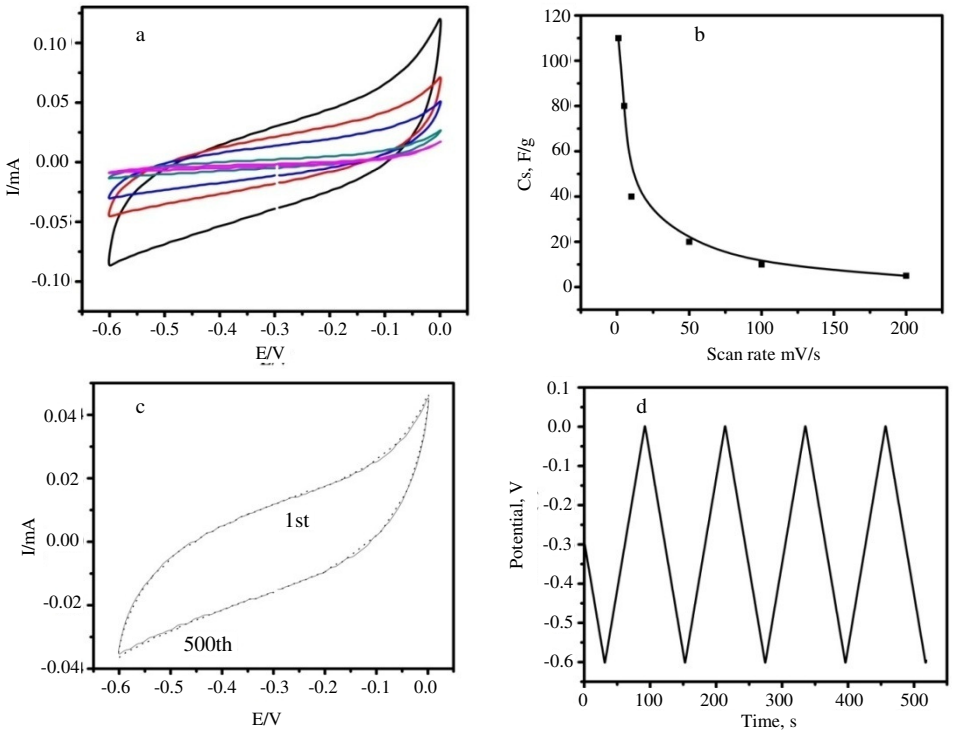

Figure 4(a). Cyclic voltammetry (CV) of WC *vs* Ag/Ag$^+$ electrode at 0.001-0.2 V/s scan rate. (b) Effect of scan rate on Cs of WC. (c) CV of WC at 0.1 V/s up to 500 cycles. (d) Charge-discharge curve of WC

Conclusion

The modified polymer route method was used to synthesize WC. The formation of WC was confirmed by diversified analytical techniques. The sulphonated polysulphone binder based WC electrode was fabricated to study the electrochemical characteristics. The electrochemical performance of WC has been examined through CV and the Cs calculated from I/V curve is 110 F/g @ 0.001 V/s. The charge-discharge curve depicts good electrochemical behavior.

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References

1. Chen T and Dai L, *Materials Today,* 2013, **16(7-8),** 272-280; DOI:10.1016/j.mattod.2013.07.002
2. Kötz R and Carlen M, *Electrochimica Acta,* 2000, **45(15-16),** 2483-2498; DOI:10.1016/S0013-4686(00)00354-6
3. Simon P and Gogotsi Y, *Nature Materials,* 2008, **7(11),** 845-854.
4. Manthiram A, Murugan A V, Sarkar, A, and Muraliganth T, *Energy Environmental Science*, 2008, **1(6),** 621-638; DOI:10.1039/B811802G
5. Pande P, Rasmussen P G and Thompson L T, *Journal Power Sources,* 2012, **207,** 212-215; DOI:10.1016/j.jpowsour.2012.01.028
6. Oyama S T, *Catalysis Today*, 1992, **15(2),** 179-200; DOI:10.1016/0920-5861(92)80175-M
7. Oyama S T, Springer, Dordrecht, 1996.
8. Claridge J B, York A P, Brungs A J and Green M L, *Chem Maters.*, 2000, **12(1),** 132-142; DOI:10.1021/cm9911060
9. Li P, Liu Z, Cui L, Zhai F, Wan Q, Li Z, Fang Z Z, Volinsky A A and Qu X, *Int J Hydrogen Energy*, 2014, **39(21),** 10911-10920; DOI:10.1016/j.ijhydene.2014.04.173
10. Palanker V S, Sokolsky D V, Mazulevsky E A and Baybatyrov E N, *Electrochimica Acta*, 1977, **22(6),** 661-667; DOI:10.1016/0013-4686(77)85136-0
11. Jeong I, Lee J, Joseph K V, Lee H I, Kim J K, Yoon S and Lee J, *Nano Energy*, 2014, **9**, 392-400; DOI:10.1016/j.nanoen.2014.08.010
12. Zhu W, Ignaszak A, Song C, Baker R, Hui R, Zhang J, Nan F, Botton G, Ye S and Campbell S, *Electrochimica Acta*, 2012, **61,** 198-206; DOI:10.1016/j.electacta.2011.12.005
13. Mudila H, Zaidi M G H, Rana S, Joshi V and Alam S, *Int J Chem Analytical Science,* 2013, **4(3),** 139-145; DOI:10.1016/j.ijcas.2013.09.001
14. Goel S, Mazumdar N A and Gupta A*, J Nanosci Nanotechnol.,* 2011, **11(11),** 10164-10172; DOI:10.1166/jnn.2011.4993
15. Cheong Y K, Calvo-Castro J, Ciric L, Edirisinghe M, Cloutman-Green E, Illangakoon U E and Ren G, *Nanomaterials*, 2017, *7***(7),** 152; DOI:10.3390/nano7070152
16. Delichere P, Falaras P, Froment M, Hugot-Le Goff A and Agius B, *Thin Solid Films*, 1988, **161,** 35-46; DOI:10.1016/0040-6090(88)90233-7
17. Pfeifer J, Guifang C, Tekula-Buxbaum P, Kiss B A, Farkas-Jahnke M and Vadasdi K, *J Solid State Chem.*, 1995, **119(1),** 90-97; DOI:10.1016/0022-4596(95)80013-F
18. Liu C, Zhou D, Zhou J, Xie Z and Xia Y, *RSC Advances*, 2016, **6(80),** 76307-76311; DOI:10.1039/C6RA12545J