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Electrical and electrochemical properties of tungsten carbide

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Abstract
Modified polymer precursor method was used to synthesized Tungsten carbide (WC). The formation of WC was ascertained through X-ray Diffraction (XRD) and Thermo Gravimetry Analysis (TGA). The WC electrode was synthesized over 316 stainless steel to evaluate electrical conductivity by four probe method and electrochemical performance through cyclic voltammetry (CV). The CV curves of WC electrode were found in the potential span of -1.5 to 0.0V in KOH (1.0M). The WC electrode exhibit band gap of 0.64 eV and good cyclic stability over 200 cycles.

Keywords: Tungsten carbide, electrical conductivity, cyclic voltammetry, cyclic stability

Introduction
Carbon, nitrogen and oxygen atoms are easily dissolve in the interstitial sites of early transition metal lattices. Their resultant alloys are identified as metal carbides, nitrides and oxycarbides respectively [1]. In recent years, tungsten carbide (WC) and its composites, titanium and nickel based alloys and other super alloys, have been synthesized to investigate their properties and applications [2]. Among these, WC is mostly studied due to exceptional physical and chemical properties [3]. WC demonstrate high melting point, good conductivity and low value of friction coefficient[4]. Therefore, tungsten carbides are used for industrial purposes like making rocket nozzles, abrasion-resistant coatings, cutting and drilling bits [4, 5]. Due to good electrical conductivity, WC and other metal carbides are used in sensors, fuel cells and catalyst applications [6-10].
The carbides of Ti to Cr group, exhibit Platinum like catalytic properties. Therefore, WC is used as electrocatlyst in anodic potential due to its prolonged stability in acid solution [11]. The blending of carbon in tungsten, make WC highly catalytic, selective and resist to poisioning. Therefore, WC can be used as catalyst for organic reactions like hydrodenitrogenation, hydrodesulfurization, alkane isomerization and other hydrocarbon conversion reactions [12].
In the present investigation, we examine the electrical and electrochemical property of WC based electrode and calculate the band gap through cyclic voltammetry.

Materials and Methods
Starting Materials
Ammonium met tungstate (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
WC was synthesized according to the protocol [13]. Typically, AMT (5.00 g) and resorcinol (1.25 g) were dissolved in formaldehyde (1.65 ml) and de-ionized water (20 ml). The resultant solution refluxed upto 90 °C for 24 hours. Then precipitate of WC was washed with de-ionized water and dried at 50±1 °C/400 mm Hg over 24 hours.

Preparation of the Working Electrodes
The metallic substrates for electrode ($2cm^2$) 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 (100µL) an ultrasonically prepared suspension comprising electroactive material (65 mg), graphite (10 mg) and SPS in NMP (5g/dL) over SS substrate. The treated electrodes were dried at room temperature for 8 hrs, followed by 60 ºC/400 mm Hg for 48 hrs. This has afforded electrodes with a mass thickness of electroactive materials by 0.04±0.01 mg [14, 15].

Characterization

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. Thermo-oxidative stability was investigated through TG and DTA over EXSTAR TG/DTA 6300 instrument in static air at a heating rate of 10ºC/ minutes a flow rate of 200 mL/min in the temperature up to 700ºC. Electrical conductivities at room temperature were performed using Keithley four-point probe DC conductivity meter equipped with 6221 DC current source and 2182A Nano voltmeter. 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 1mA in the range of -1.5 to 0.0V, at 0.001-0.05 V/s at ambient temperature.

Results and Discussion

XRD Spectra

The XRD spectra of WC are shown in figure 1. The diffraction peaks confirm the crystalline nature of synthesized WC. Three major intense diffraction peaks are shown at 31.49°, 35.70° and 48.35° correspond to [001],[100] and [101] (JCPDS 73-0471) respectively [16].

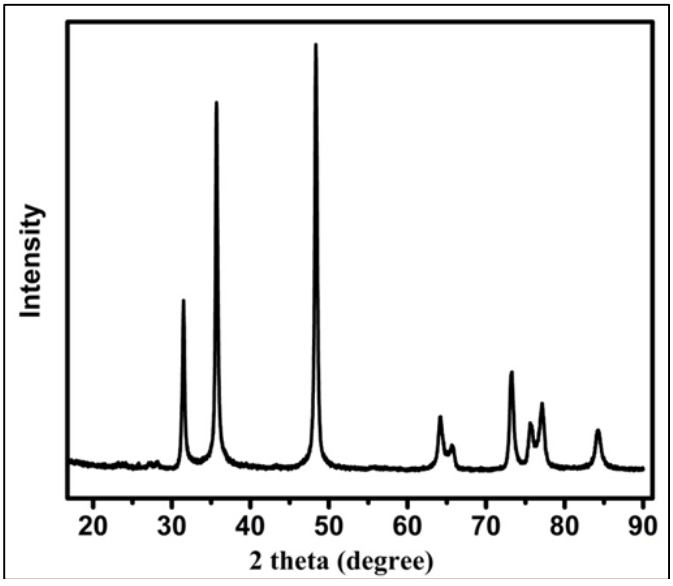

Fig 1: XRD spectra of WC

Thermal Stability

Figure 2, exhibit the TG of WC. WC was thermally stable up to 384 ºC. WC was decaying with TG onset at 528 ºC. This was accompanied with weight gain of 4.90 % due to oxidation [18]. The TG endset of WC was appeared at 597 ºC leaving char residue of 114.70 wt % [16].

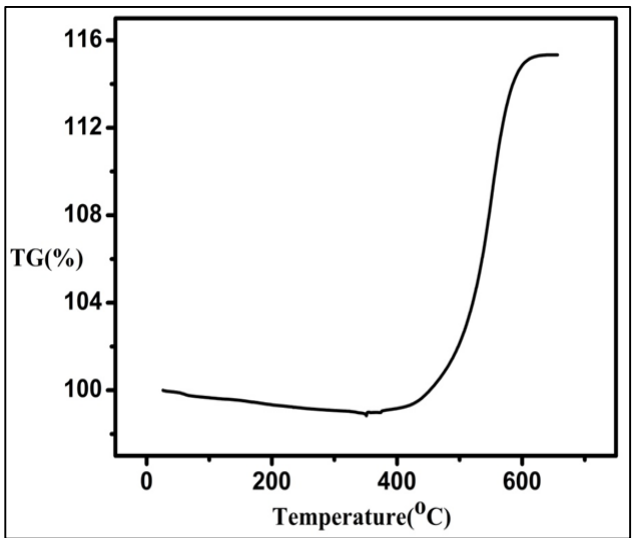

Fig 2: TG curve of WC

Electrical Conductivity

DC conductivity of WC was investigated through four probe conductivity method. The conductivity (σ X 10^5 S/cm) is measured at varying voltages i.e. 1V, 10 V and 100 V (figure 3). On increasing the voltage from 1 to 100 V, σ increases from 0.32 to 1.50 respectively at room temperature. Therefore, the enhancement in the value of σ with voltage, confirm the semiconducting behavior of WC.

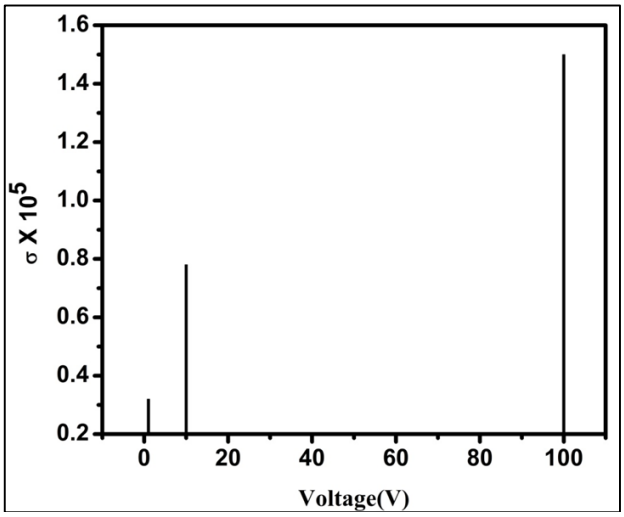

Fig 3: Conductivity of WC at 25 ^{O}C

Electrochemical Behavior

The electrochemical behavior of WC was analysed through cyclic voltammetry (CV). WC show redox behavior in the full window range (-1.5 to 0.0 V) of CV (figure, 4a). The redox peaks were observed due to the transition between the semiconducting and the conducting state. The shift in peak potential with scan rate is probably due to slow ion diffusion or interfacial charge transfer process [17].

Cyclic voltammetry was also used to find the energy gap between the HOMO and LUMO energy levels by using the oxidation and reduction potentials of WC. The band gap (Eg) was found by using formula: Eg = LUMO - HOMO, where HOMO = - (E_{ox} (onset) + 4.4) eV and Ea = - (E_{red} (onset) + 4.4) eV [18]. From the cyclic voltammogram at 25 V/s, the values of onset oxidation and reduction potentials for WC were -0.73 and -1.37 (figure, 4b). The electrochemical band gap for WC is 0.64 eV. Thus, conclude the good

electrochemical performance of WC due to easier transfer of electron between the valence and conduction band.

Further to investigate, the cyclic stability of WC, the scan were run upto 200 cycles at scan rate of 25 V/s (figure, 4c). The WC electrode show negligible loss of specific capacitance at the end of the cycles. The charge-discharge curve are also linear without any deviation in slope in the same window range, suggest good electrochemical stability of the electrode (figure, 4d).

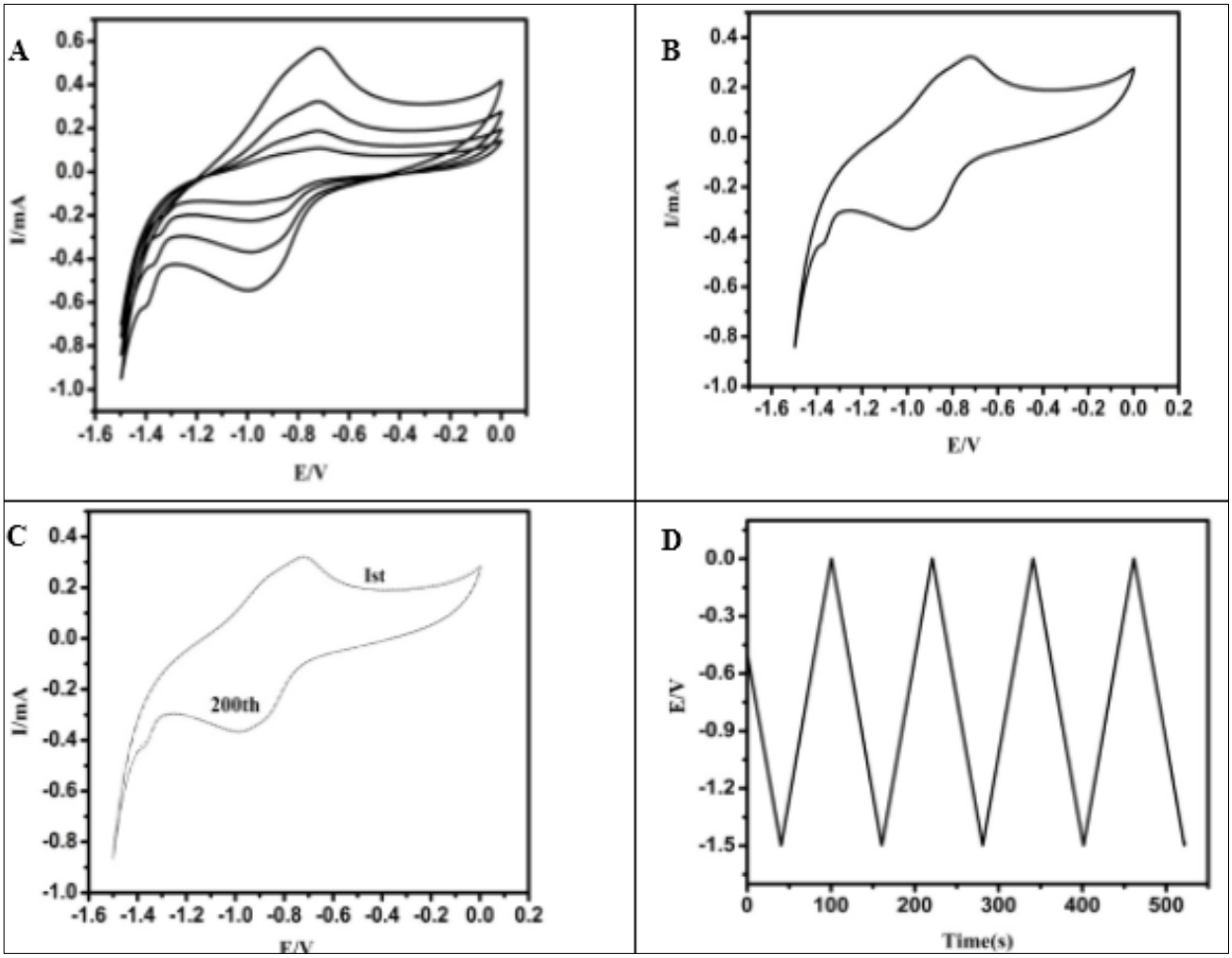

Fig 4: (a) CV curve of WC at 0.001-0.05 V/s scan rate, (b) Cv of WC at 0.025 V/s, (c) Cyclic stability of WC upto 200 cycles, (d) charge-discharge curve of WC.

Conclusions

The WC was synthesized by modified polymer route method. The synthesized WC was confirmed by diversified analytical techniques. The sulphonated polysulphone binder based WC electrode was fabricated to study the electrical and electrochemical characteristics to evaluate the band gap. The band gap of WC electrode is 0.64 eV at 25 V/s. The cyclic stabilty of WC has been examined through CV. The charge-discharge curve depicts good electrochemical behavior.

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