Synthesis and characterization of Ni2C: An efficient electrocatalyst towards hydrogen evolution reaction

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Research Article

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Abstract

Ni_2C electrocatalyst were synthesized and characterized for the Hydrogen Evolution Reaction (HER) electrolyzer. One step hydrothermal technique is used to synthesize Ni_2C sample. Platinum based electro catalyst materials are initial and best electro catalyst for Hydrogen Evolution Reaction (HER). Ni_2C (Nickel Carbide electro catalyst) was examined by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD). Electrochemical characterization like cyclic voltammetry (CV), Tafel polarization and electrochemical impedance spectroscopy (EIS) studies is employed to explore the elctrocatalytic behavior of Ni_2C material for HER. FTIR study confirms the presence of Ni_2C electrocatalyst by the presence of metal peaks and various functional groups. The isomeric nature and purity of synthesized material were explored by powder X-ray diffraction studies. Cyclic voltammetry technique was performed in 0.5 M H_2SO_4 solution to attain the polarization curve of Ni_2C electrocatalyst for HER.

Introduction

Energy is incredibly necessary to our day to day life. Energy exists in many forms like heat, kinetic or energy, light, potential and power, or alternative forms [1–3]. As we tend to target element energy, the uses of element greatly scale back pollution. Once element is combined with gas in an exceedingly electric cell, energy within the variety of electricity is made. No greenhouse gasses or alternative particulates square measure made by the employment of element fuel cells. If element is made from water we've a property production system. Water splitting method is directed through electrolysis reaction. During this method, Hydrogen and Oxygen are separated by dipping the electric charge in water. Power electrolyzers is a common renewable energy to store the element from water. Victimisation energy provides a property of freelance of fossil oil merchandise and it is nonpolluting. Once the element is made in Associate in nursing electrolyzer it is often utilized in an electric cell to provide electricity. The byproducts of the electric cell method square measure water and warmth [4, 5].

Water can be converted to gas and gas in electrolysis by applying an electrical current. The desirable electricity may be made oppression to any range of resources. However, to attenuate greenhouse emission emissions, gas may be made employing a kind of resources together with biomass, hydro, wind, solar, geothermal, nuclear, coal with carbon capture, utilization and storage, and gas. This diversity of sources makes gas a promising energy carrier and allows gas production virtually any place within the world [6]. Water electrolysis has for many years provided hydrogen and oxygen on demand for a number of customers in various industries around the world. This provides a profitable business platform for manufactures of the technology and is funding development of electrolysers to enable their deployment in the renewable energy sector [7, 8].

“Electrocatalysts ar a selected kind of catalysts that operate at conductor surfaces or is also the conductor surface itself. Associate degree electrocatalyst is heterogeneous like a Pt surface or nanoparticles, or consistent sort of a coordination advanced or catalyst. The electrocatalyst contributes in transferring electrons between the conductor and reactants, also associate degreed facilitates and associate degree intermediate chemical transformation delineate by an overall 0.5 reaction" [9]. Catalyst materials modify and increase the speed of chemical reactions while not being consumed within the method [10]. It results the reaction to lower their energy through a distinct path. High surface area, larger activation centers are the ability of the catalyst in increasing the reactivity [11]. The first step in HER is to discharge H_3O^+ hydrogen ion concentration to supply an atom that is absorbed on the catalyst's surface (Volmer reaction). The second step can be two different reactions. One is that the chemistry action step, that is understood because the chemist reaction. The opposite doable pathway is that the Tafel recombination reaction involving two adsorbable chemical element atoms [12]. Platinum-based materials are the square measure to make simple electrocatalyst for chemical element Hydrogen Evolution Reaction (HER). Thanks to their scarce and high expenses at this time, the high potency and low price of electro catalysts square measure still difficult in HER. Therefore the future development of highly active electrocatalysts of HER is mainly focused on materials which are highly active, low cost and abundantly available [13–15].

Scope And Objectives

The world consumes more and more fossil fuels and the global climate becomes warmer and warmer. Hydrogen is considered as an alternative fuel, it is the friendliest fuel to the environment; it has the largest energy density, hydrogen fuel production has gained increased attention as oil and other non-renewable fuels become increasingly depleted and expensive. Therefore, the analysis focus of element production in water electrolysis is principally on the way to cut back the consumption. Mostly Pt based materials are a square measure which is the most effective electrocatalyst for element Evolution Reaction (HER). Because of their scarce and high expenses at this time, high potency and low value of electrocatalysts square measure is still difficult in HER. Therefore the future development of highly active electrocatalysts of HER is mainly focused on materials which are highly active, low cost and abundantly available,

Hydrothermal method is used to investigate the synthesized Ni2C electrocatalyst. The objectives of this work has summarized by, (i) to synthesize the selective low cost Pt free Ni_2C electrocatalyst by using a simple one step hydrothermal method. (ii) to characterize the synthesized material mistreatment numerous techniques like, Fourier transform infrared (FT-IR) spectrometry, X-ray diffraction (XRD), Cyclic voltammetry (CV), Tafel polarization studies. (iii) to explore the low price and high electro chemical activity of Ni_2C materials for HER.

Materials And Methods

Materials required

Nickel chloride hexahydrate ($NiCl_2.6H_2O$), Melamine ($C_3H_6N_6$), Glucose ($C_6H_{12}O_6.H_2O$), Absolute ethanol (C_2H_5OH), Hydrazine hydrate ($NH_2NH_2.H_2O$). All chemicals are purchased from Nice Chemicals, India.

Synthesis of Ni_2C by hydrothermal method

The Ni_2C electrocatalyst were synthesized by hydrothermal method. 20 mmol of Nickel chloride hexahydrate ($NiCl_2.6H_2O$), 10 mmol of Melamine ($C_3H_6N_6$), and 20 mmol of Glucose ($C_6H_{12}O_6.H_2O$) were diversified in 30 mL deionized (DI) water and 20 mL of ethanol, the solution is ultra-sonicated for 30 min. The Ni_2C sample is placed in Teflon-autoclave (100 mL) for hydrothermal reaction, the mixture is calcinated in muffle furnace for 12 hr at 200°C. Then precipitate was sieved using whatman filter paper and washed with Deionized water and ethanol for several times and it is dried using hot air oven at 80°C for 3 hr. Then, the precipitate was calcined at 500°C using a tubular furnace for 3 hr in N_2 atmosphere. Finally, obtained black color precipitate of Ni_2C is further used for characterizations and electrochemical analysis. The clear schematic methodology which is given in Fig. 1.

Preparation of working electrode

Typically, 5 mg of catalyst was dispersed in a clean mortar and add 1mg of carbon black, these are mixed and grained well for 1min. and add 1mg of Poly Vinyl difluride (PVDF) and again grained for 1min latter add 1 drop of n-methyl pyrrolidone (NMP) and all mixtures are grained well and coated on the marked area (0.5 cm^2) on the carbon sheet and it is placed in hot air oven for 1 hr which is preserved at 60° C.

Electrochemical measurements

Electrochemical analysis is carried on CHI608E electrochemical workstation to evaluate the HER activity of synthesized Ni_2C electrocatalyst by employing a typical 3-electrode system are working electrode, counter electrode and reference electrode. Carbon sheet (working electrode), platinum (Pt) electrode (counter electrode), and Ag/AgCl (sat.KCl) electrode (reference electrode). All electrochemical tests were done using electrolyte with 0.5 M H_2SO_4. To perform the HER analysis, the electrode was scanned for ten cycles via cyclic voltammetry (CV). Tafel studies was measured at scan rate of 2 mVs^{-1}, and Electrochemical impedance spectroscopy (EIS) analysis was performed with superimposing signals in the frequency range from 106 to 10 Hz with amplitude at 5 mV.

Results And Discussions

FT-IR studies

Fourier infrared spectrometer (FTIR) is an analytic technique used to explore the functional groups present in the synthesized Ni_2C sample in the range of 400 to 4000 cm^{-1}. FT-IR absorption spectrum of as synthesized Ni_2C electro catalyst is displayed in Fig. 2. A strong peak at 3565 cm^{-1} is due to presence of water and peak appearing at 2921 cm^{-1} it is an asymmetric stretching vibrations of C–H bond, the peaks at 1605 cm^{-1} and 1395 cm^{-1} is analogous to C–O stretching vibration. 837 cm^{-1} and 731 cm^{-1} are the strong absorption band which confirms the metal stretching vibration modes in Ni_2C sample.

X-ray Diffraction studies

Nature and the structure of the sample can be identified by X-ray diffraction pattern.. The XRD pattern for Ni_2C electrocatalyst is displayed in Fig. 3. The Ni_2C have different diffraction peaks at 2θ values 23.5°, 34.2°, 41.5°, 47.2°, 53.1°, 58.5°, and 69.3° were indexed to (100), (200), (101), (102), (001), (220), and (111) respectively. These planes are indicates the cubic phase crystalline structure of the synthesized Ni_2C electrocatalyst and these results are well correlated with the JCPDS: 06-0693 patterns. These results confirmed the formation of Ni_2C electrocatalyst with a cubic phase crystalline structure by hydrothermal synthesized method.

Electrocatalytic activity towards HER

CV studies

cyclic voltammetry technique is used to evaluate the catalytic activity in HER of the Ni_2C electrocatalyst, was performed in 0.5M sulfuric acid solution at 2 mVs^{-1} scanning rate in room temperature. Fig. 4. shows the CV polarization curve for Ni_2C electrocatalyst. The results of the polarization towards the HER show the peak with high current density at low over potential value. Ni_2C electrocatalyst exhibits current density at 17mA/cm^2 in 250 mV fixed potential and similarly, the over potential value is 203 mV at fixed current density 10 mA/cm^2. Hence, these values' signifying the prepared Ni_2C has having the admirable HER activity.

Tafel studies

Tafel slope yields the electrocatalytic HER performance of Ni_2C electrocatalyst. As shown in Fig. 5, the Ni_2C electrocatalyst has achieved a small tafel slope at 93 mV/dec, It specify that the smaller Tafel slope of the Ni_2C sample, the higher the HER activity. The Tafel plot (Fig. 5) is fitted by following Tafel equation is,

$\eta = b \times \log j + a$ (1)

Where, η - over potential (mV),

j - Current density ($mA{\cdot}cm^{-2}$). ~93mV/dec is the calculated slope value of Tafel

The Tafel slope revealed that the HER catalyzed by Ni_2C electrocatalyst occurs through the mixed Volmer mechanism. Tafel slope in Fig. 5 is due to the quicker proton discharge kinetic and shows superior HER activity in Ni_2C electrocatalyst. In classic theory, HER at acidic aqueous media can be proceeds through two steps as shown below,

The first step is to electrochemical reduction (H^+ reduction, Volmer-reaction)

$H_3O^+ + e^- \rightarrow H_{ad} + H_2O$ (118 mV/dec) (2)

The second step (H_{ads} desorption) is moreover the ion and atom reaction (Heyrovsky-reaction)

$H_{ad} + H^+ + e^- \rightarrow H2$ (40 mV/dec) (3)

The atom combination reaction (Tafel-reaction)

$H_{ad} + H_{ad} \rightarrow H_2$ (30 mV/dec) (4)

The Tafel slope is insufficient to determine the precise mechanism, also the reduced slope in Ni_2C sample confirms the promoted Volmer-step in hydrogen evolution reaction mechanism.

EIS analysis

The EIS measurements were performed to evaluate the electrocatalytic activity of the Ni_2C electrocatalyst and also the corresponding Nyquist plot is displayed in Fig. 6. The charge transfer resistance was investigated carried throgh EIS analysis. The Ni_2C catalyst exhibit a lower Rctvalue (54 Ω) indicate that the synthesized Ni_2C electrocatalyst has a high electronic conductivity. EIS analysis shows the high electrochemical enactment in Ni_2C sample. It may be seen that the EIS measurements are in sensible agreement with the results discovered from cyclic voltametry analysis.

Conclusion

In summary, we have designed and developed the Ni_2C electrocatalyst by a simple one step hydrothermal method followed by calcination. In acidic medium the Ni_2C electrocatalyst act as associate electrocatalyst towards the HER. Electrochemical analysis results the Ni_2C electrocatalyst parades an ideal HER performance with a low overpotential of 203 mV at 10 mA cm^{-2} the fixed current density, the Tafel slope ensues low as 93 mV/dec. The synthesized Ni_2C shows a lower Rctvalue (54 Ω) indicate the high electronic conductivity of electrocatalyst in EIS analysis. The as-synthesized Ni_2C catalysts have excellent and adjustable HER activities. Our preliminary results demonstrate the many influence of artificial condition on the structure and catalytic performance of the catalyst. This study confirms the great potential of Ni_2C as an alternative to Pt-group metals for hydrogen generation through water splitting, and provides new perceptions into the structure control and performance enhancement of Ni_2C-based electrocatalysts.

Declarations

Competing interests: The authors declare no competing interests.

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Figures

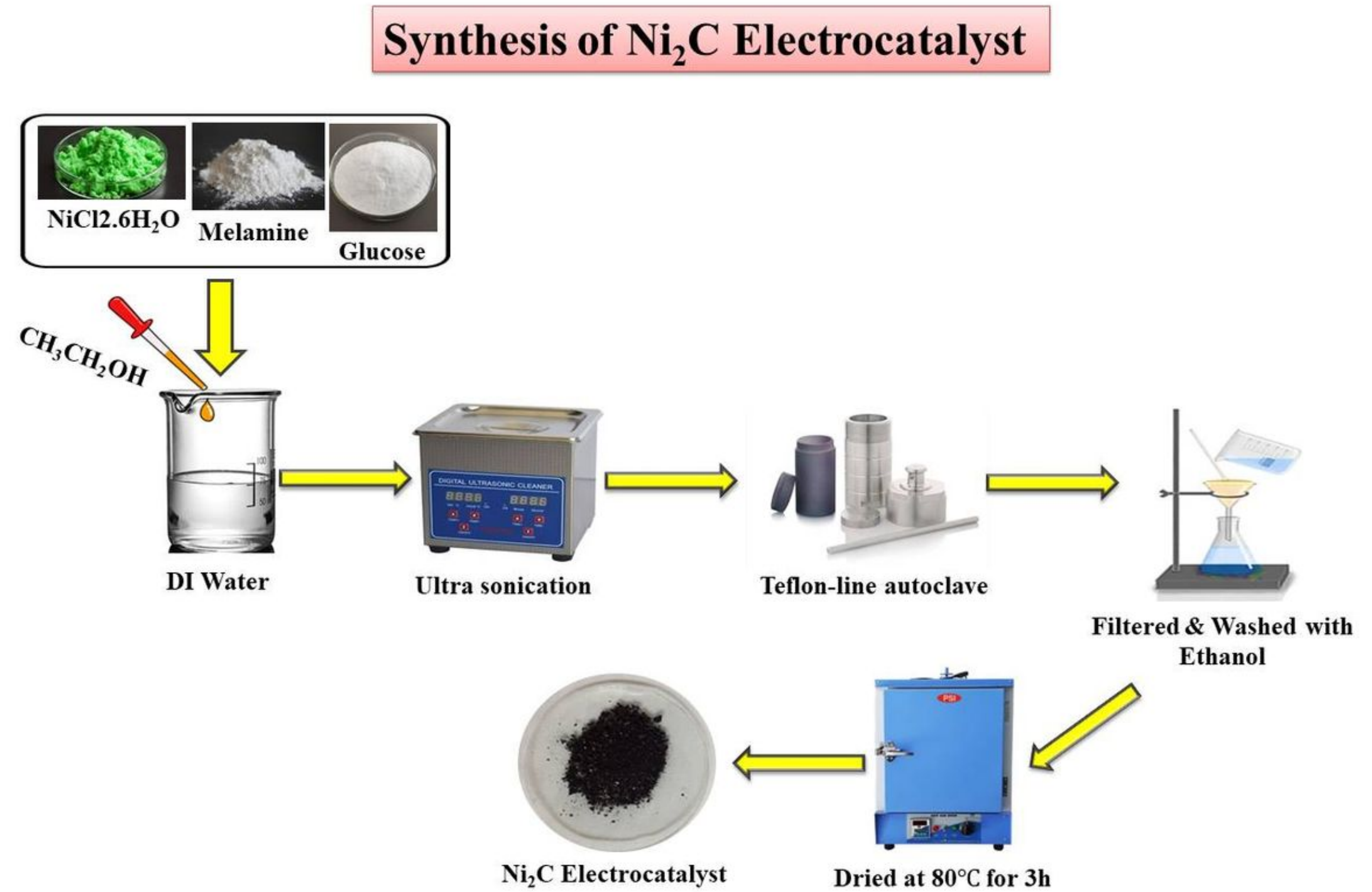

Figure 1

Schematic methodology of Ni2C electrocatalyst

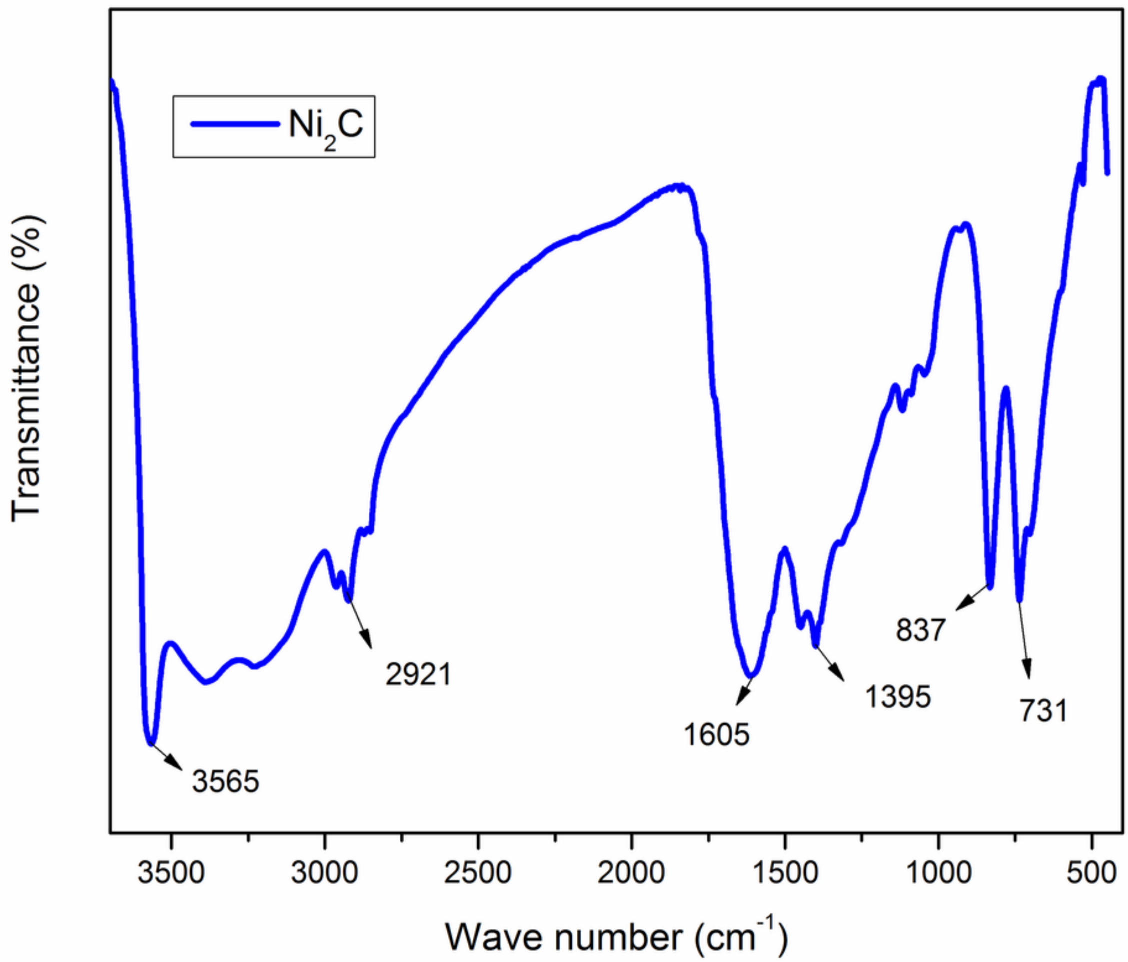

Figure 2

FT-IR spectrum of synthesized Ni2C electrocatalyst

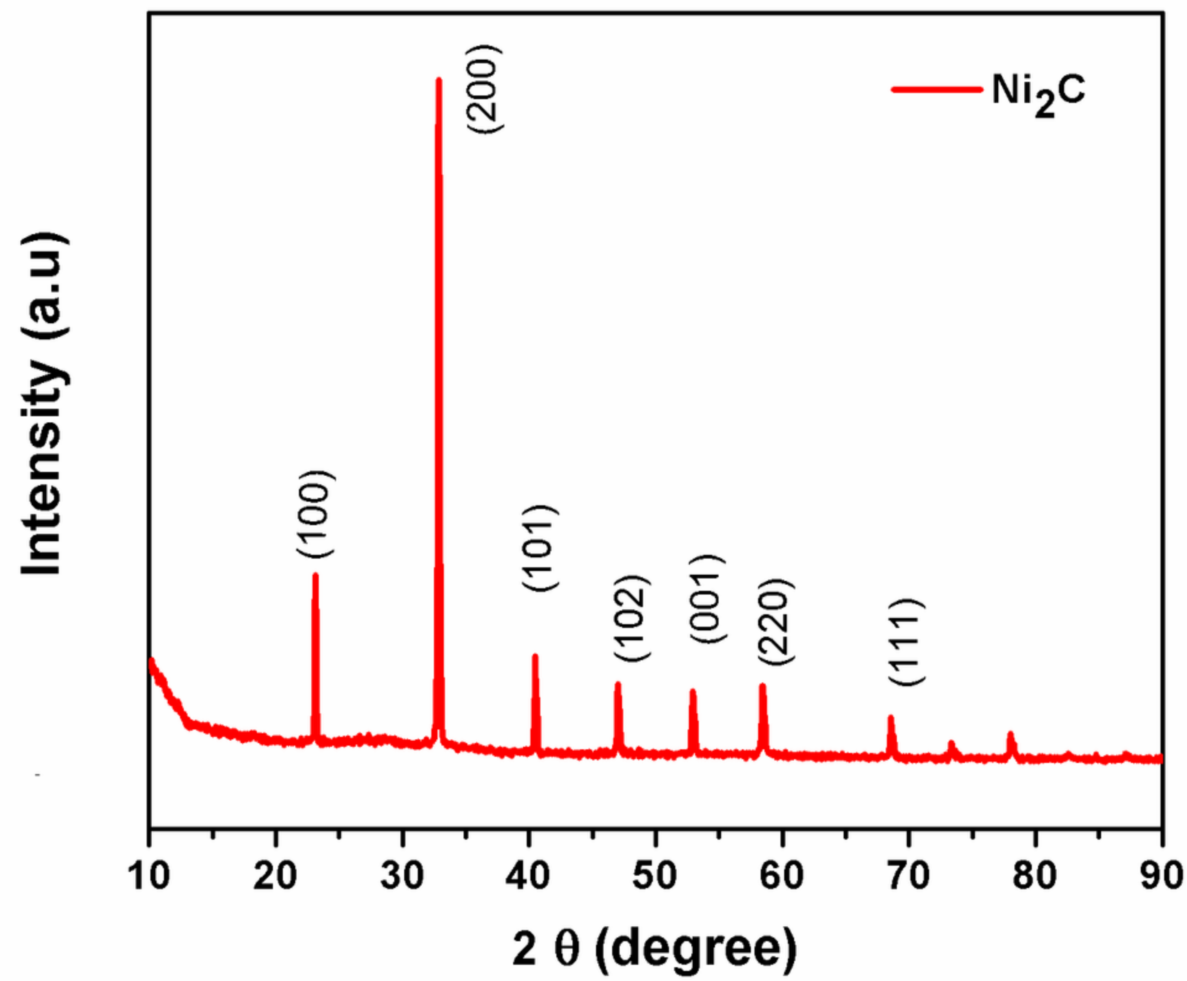

Figure 3

XRD pattern of Ni2C electrocatalyst

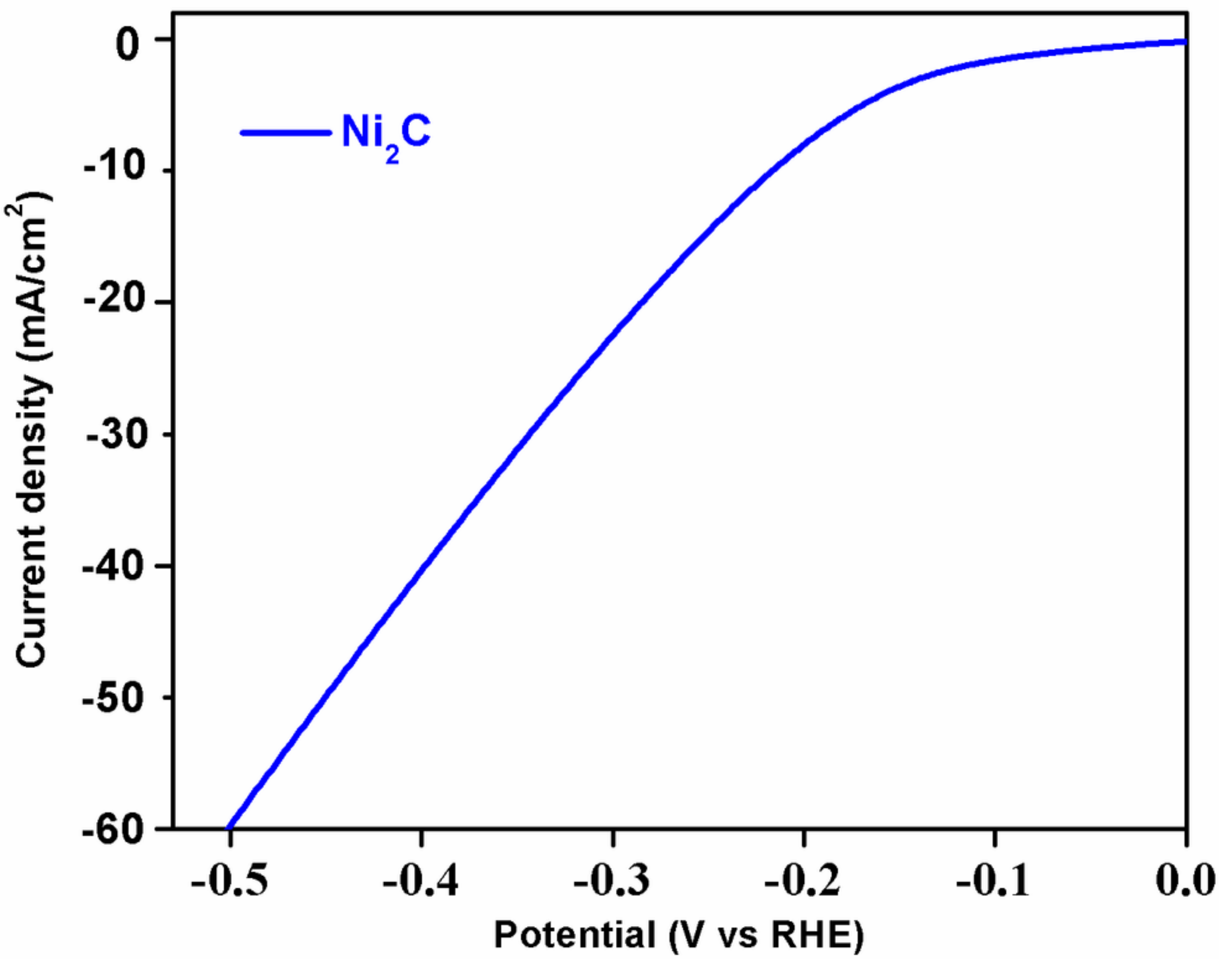

Figure 4

CV polarization curve of Ni2C electrocatalyst

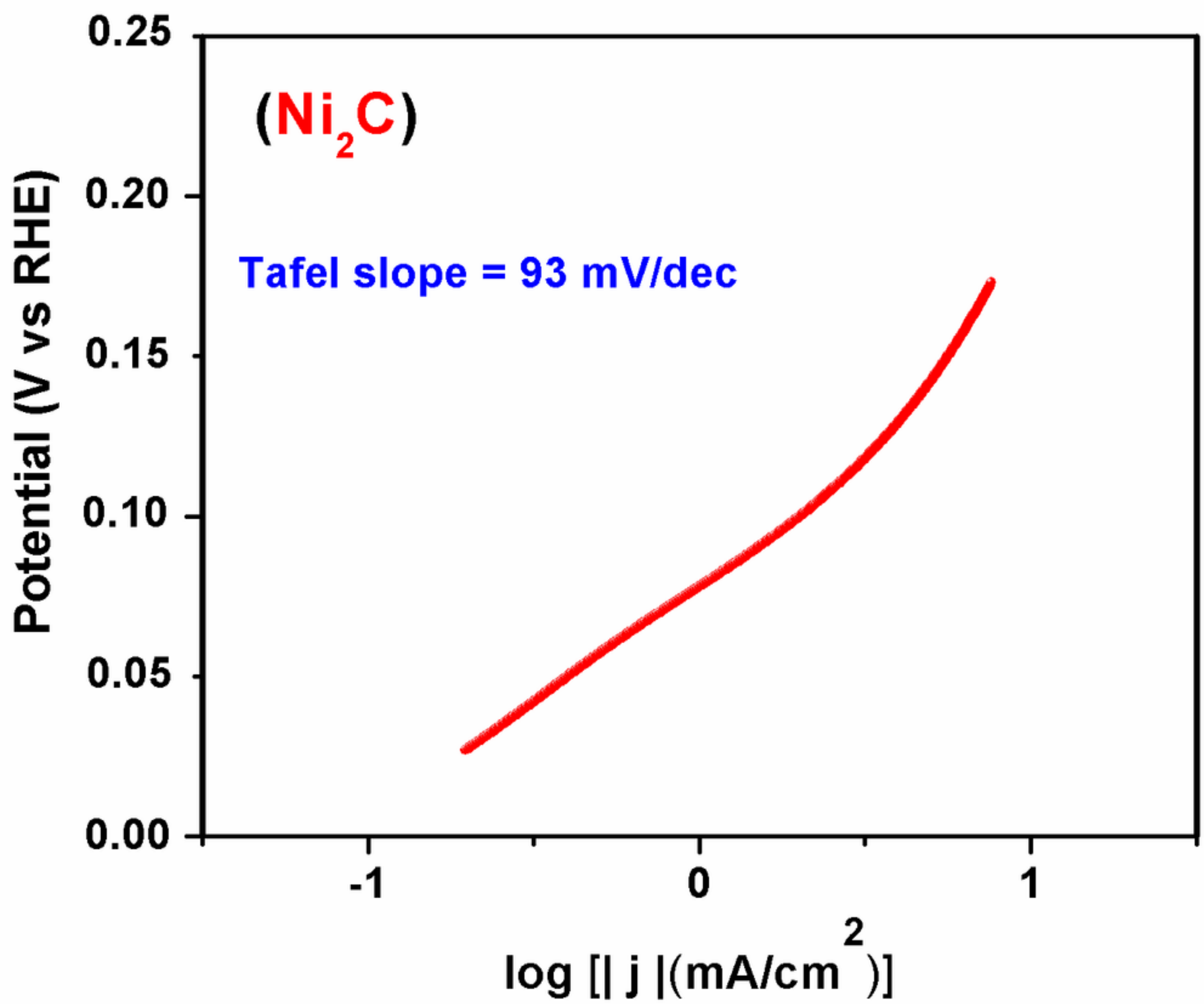

Figure 5

Tafel slope for the synthesized Ni2C electrocatalyst

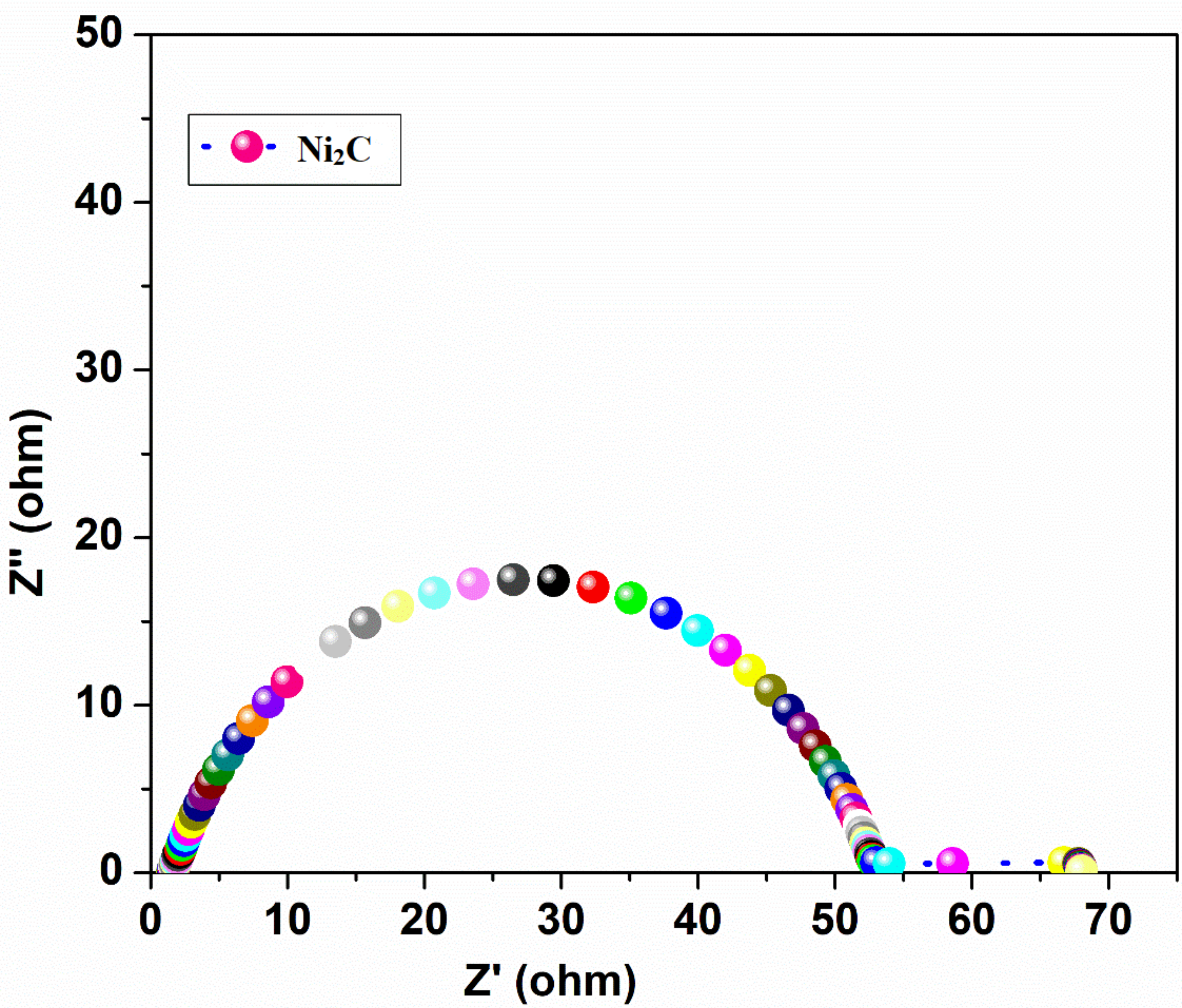

Figure 6

The Nyquist plot of Ni2C