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ELECTROCHEMICAL STUDY OF COPPER OXIDE USING DIMETHYLIMIDAZOLIUM BASED IONIC LIQUID

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Abstract
We have studied 0.1 M 1-(1'-methyl-2'-oxo-propyl)-2,3-dimethylimidazolium chloride [MOPDMIM] [Cl] ionic liquid electrolyte with the hydrothermally synthesized copper oxide obtained from aqueous copper sulphate precursor solution for supercapacitor application. As synthesized CuO electrode was characterized by Fourier transform infrared (FTIR), X-ray diffraction technique (XRD) and scanning electron microscopy (SEM). Electrochemical studies of CuO were carried out with respect to cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS). The specific capacitance obtained was 69 F/g at 10 mV s^{-1}.

Keywords: Ionic liquid, Hydrothermal, Copper oxide, Electrolyte

Introduction

Most effective and practical devices used for energy conversion and energy storage are batteries, fuel cells and super capacitors (SCs). Due to high power density, high specific power and long life cycle, SCs attracted significant attention in various applications. Electrode and electrolyte are the important constituents of the SCs which are responsible for the performance of the SC. Thus, searching novel electrolytes having wide electrochemical window is a continuous process because the energy of SC is proportional to the squared maximum voltage [1]. Electrolytes must have high purity, high conductivity, wide potential window, high stability, low toxicity, low cost, and low solvated ionic size. Among the three types of electrolytes, aqueous electrolytes have the range of potential window 1.2 V that limits cell voltage and thus limiting power density and energy density of SC. Hence organic electrolytes are often recommended as they are stable enough over wide range of potential window of 3.5 V, However, they create environmental problems and safety hazards as they are flammable, volatile and toxic. Ionic liquids (ILs) which fulfill the requirements of electrolytes such as wide electrochemical window (2 to 6 V) and conductivity of 10 mS^{-1}[2]. The more attention of ILs is because of non-volatility, non-flammability, high thermal and electrochemical stability, high charge mobility [3, 4] and non-toxicity. This attracted huge interest of the researchers towards ILs in various applications [5].

Electrochemical properties of ILs mostly depend on the type of cations and anions. Thus by choosing proper ions one can design the IL hence ILs are also called as designer solvents. Di Wei et al [6] introduced ecofriendly SC based on 1-butyl-3-methylimidazoliumchloride (18 F/g), Shaikh et al reported 3-carboxymethyl-1-methylimidazolium bisulphate IL and used for SC application, Navathe et al [7] used [HPMIM][Cl] IL for SC application this shows that the use of ILs in electrochemistry is increasing day by day.

In the present work, we report the supercapacitor application of 0.1 M solution of [MOPDMIM][Cl] IL electrolyte with the hydrothermally synthesized copper oxide CuO.

Experimental

All the chemicals used for the synthesis were of analytical grade and used without further purification.

Synthesis of 1-(1'-methyl-2'-oxopropyl)-2,3-dimethylimidazolium chloride [MOPDMIM][Cl] ionic liquid

A [MOPDMIM][Cl] IL was synthesized by solvent free method as reported by earlier method and its 0.1 M aqueous solution was used as an electrolyte for supercapacitor application. The structure of which is represented as below:

Synthesis of copper oxide

Nanostructured CuO was prepared from 0.1 M copper sulphate ($CuSO_4$) precursor solution on stainless steel (SS) substrate by hydrothermal method as reported earlier [7].

Characterization Techniques

The Fourier transform infrared (FTIR) spectrum of the prepared electrodes was recorded with a FTIR spectrometer (Perkin Elmer) in the scanning range 500-3000 cm^{-1}. The structural and surface morphology of CuO was studied using X-ray diffractometer (XRD, Bruker D2 Phaser) and scanning electron microscope (SEM, JEOL JSM 6360). The electrochemical performance was evaluated by using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) in 0.1 M [MOPDMIM][Cl] IL electrolyte in three electrode system consisting CuO electrode as working electrode, saturated calomel electrode (SCE) as reference electrode and graphite as current collector electrode using Autolab PGSTAT302 potentiostat/galvanostat equipped with a FRA 2 module.

Results and discussion

FTIR analysis

FTIR spectrum (Fig. 1) shows bands in the wave number range of 500-3000 cm^{-1}. The two prominent bands at 524 and 608 cm^{-1} correspond to the stretching vibrations of Cu–O [8] indicating the formation of CuO.

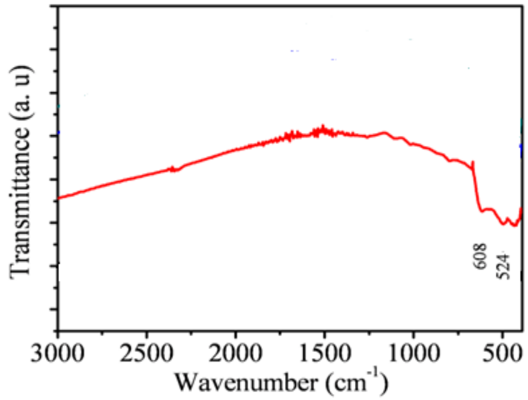

Figure 1 Infrared spectrum of CuO

XRD analysis

Fig. 2 shows the XRD pattern of CuO. It shows peaks at 35.52° and 38.19° with d_{hkl} along (11-1) and (111) planes which corresponds to CuO. The peaks at 43.19˚, 44.12˚, 50.30˚ and 74.32˚ are due to SS substrate and marked as Δ. The formation of CuO is confirmed by comparing the standard ICDD card (96-101-1149) with monoclinic crystal structure.

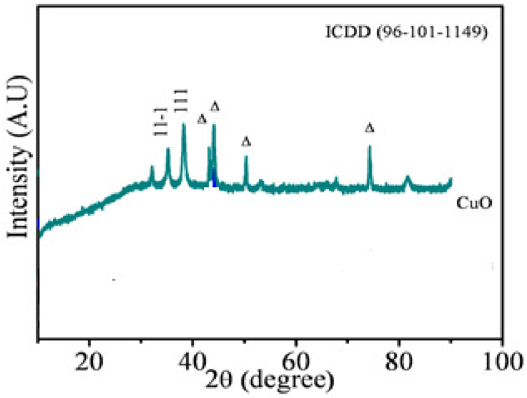

Figure 2 X-ray diffraction pattern of CuO

Scanning electron microscopy studies

Fig. 3 shows SEM image of CuO shows well crystalline bunches of petals. This may be suitable for the ions of [MOPDMIM][Cl] IL thereby reducing diffusion resistance and showing comparatively high charge-discharge rate and good specific capacitance.

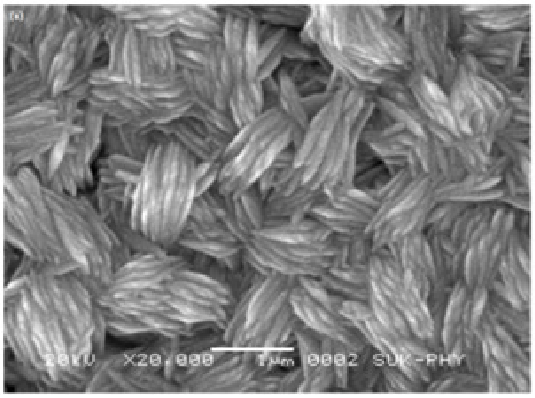

Figure 3 SEM image of CuO

Cyclic voltammetry studies

The electrochemical properties of CuO were studied by CV analysis. The pseudocapacitance of CuO is the result of redox [8] reaction as shown as below:

$Cu^{+2} + e^{-} \leftrightarrow Cu^{+1}$

CV measurements of CuO were carried out in 0.1 M aqueous [MOPDMIM][Cl] IL within the potential window of -0.6 V to 0.3 V vs. SCE at 10 mV s^{-1} as shown in Fig. 4. Specific capacitance calculated using known equation and maximum specific capacitance of 69 F g^{-1} was obtained for the CuO electrode at 10 mV s^{-1}. Inset of Fig. 4 is the plot that shows the variation specific capacitance versus scan rate indicating that, specific capacitance decreases with increase in the scan rate.

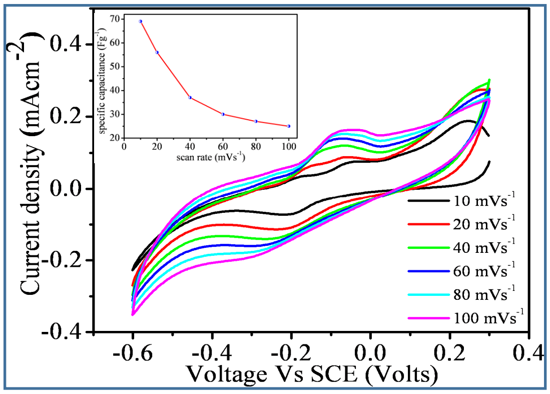

Figure 4 Cyclic voltamogramm of CuO in 0.1M [MOPDMIM][Cl] IL at different scan rate

Galvanostatic charge-discharge analysis

Charge-discharge investigation of CuO was carried out in 0.1 M [MOPDMIM][Cl] IL at 0.1 mA cm^{-2} within the potential range of -0.6 to 0.3 V as shown in Fig. 5. The curve includes charging curve ranging from 0.0 to 0.3 V due to oxidation of Cu^{+1} to Cu^{+2} and discharging curve having two regions, a fast potential drop followed by slow potential decay [10]. Each region accounts for about half of the total specific capacitance.

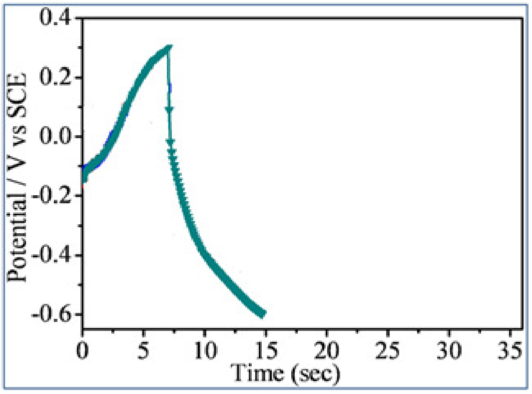

Fig. 5 Galvanostatic charge-discharge curve of CuO at 0.1mA cm^{-2} current density

Electrochemical impedance spectroscopy study

Electrochemical impedance spectroscopy study delivers the information about the behavior of ions of electrolyte and electrons of the electrode at the electrode/electrolyte interface. Fig. 6 shows the Nyquist plot of the CuO in 0.1 M [MOPDMIM][Cl] IL. The spectrum shows semicircle at higher frequency region due to parallel combination of the charge transfer resistance (Rct) [3] and a straight line at low frequency region that corresponds to Warburg impedance (Z_W) caused due to the ionic extraction/intercalation of the ions of the electrolyte in the pores of CuO.

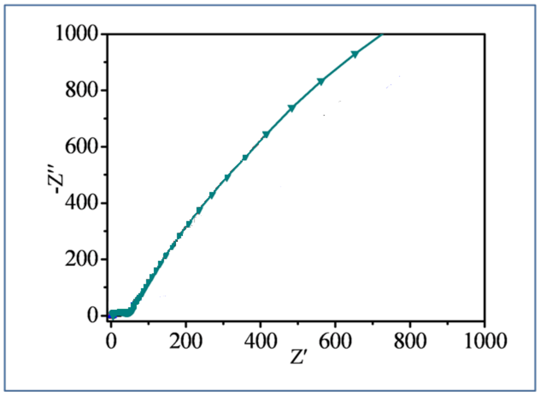

Fig. 6 Nyquist plot of CuO in 0.1 M [MOPDMIM][Cl] IL

Conclusions

In summary, the present work demonstrates preparation of CuO thin film by rapid and inexpensive hydrothermal technique from $CuSO_4$ precursor. The supercapacitive performance of the CuO was tested in [MOPDMIM][Cl] ionic liquid as an electrolyte. The electrochemical study showed specific capacitance of 69 F/g at 10 mV s^{-1}. Thus, this study concludes that, CuO with 0.1 M [MOPDMIM][Cl] IL as electrolyte is useful in developing supercapacitor with better specific capacitance.

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