Journal of Energy Storage 6 (2016) 22–31

Contents lists available at ScienceDirect

Journal of Energy Storage

journal homepage: www.elsevier.com/locate/est

In-situ hydrothermal synthesis of MnO_2/NiO@Ni hetero structure electrode for hydrogen evolution reaction and high energy asymmetric supercapacitor applications

Sanjit Saha[a,b], Suman Chhetri[a,b], Partha Khanra[c], Pranab Samanta[a,b], Hyeyoung Koo[d], Naresh Chandra Murmu[a,b], Tapas Kuila[a,b,*]

[a] *Surface Engineering and Tribology Division, CSIR-Central Mechanical Engineering Research Institute, Durgapur 713209, India*
[b] *Academy of Scientific and Innovative Research (AcSIR), CSIR-CMERI Campus, Durgapur 713209, India*
[c] *Soft Innovative Materials Research Centre, Korea Institute of Science and Technology (KIST), Jeonbuk 565905, South Korea*
[d] *Soft Innovative Materials Research Centre, Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST), Jeonbuk 565905, South Korea*

ARTICLE INFO

Article history:
Received 18 November 2015
Received in revised form 17 February 2016
Accepted 17 February 2016
Available online 27 February 2016

Keywords:
Multi-metal oxide
Binder free electrode
Hydrogen evalution reaction
Thermaly reduced graphene oxide
Asymmetric device
Energy density

ABSTRACT

In-situ deposition of MnO_2/NiO hetero structure on Ni-foam has been carried out through simple one-step hydrothermal reaction. The *in-situ* deposited multi-metal oxide shows extraordinary electrocatalytic activity in hydrogen evolution reaction with a small Tafel slope of 38 mV per decade and very low onset potential of 0.17 V. An electrolyser has been fabricated with MnO_2/NiO deposited Ni-foam which effectively achieves a current density of $\sim$24 mA cm^{-2} at an applied voltage of $\sim$1.57 V. Furthermore, the metal oxide deposited on Ni-foam is directly used as the supercapacitor electrode which shows good rate capability as positive electrode materials. An asymmetric capacitor (ASC) has been assembled by using the MnO_2/NiO deposited Ni-foam as positive electrode and thermally reduced graphene oxide as negative electrode. The assembled ASC has a large specific capacitance of 218 F g^{-1} at a current density of 3 A g^{-1} and can deliver high energy and power density of 59.5 Wh kg^{-1} and 25,350 W kg^{-1}, respectively. The ASC shows very good electrochemical stability throughout 10,000 charge–discharge cycles along with the capability to work in the high frequency range.

1. Introduction

The ever rising demand of energy accompanied with global warming and environmental deterioration has obliged us to develop an alternative source of clean energy fuel carrier [1–5]. Low pollutant emission and high efficiency make hydrogen as a future candidate for the replacement of fossil fuels [3,4]. The electrochemical splitting of water into hydrogen and oxygen is an effective technique of producing high-purity hydrogen [5]. The hydrogen evolution reaction (HER) and oxygen evolution reaction are the two half reactions of water splitting and plays crucial role for the overall efficiency [2]. Commercial electrolyzers suffer from large operating cell voltage which in turn increases the overall energy consumption resulting poor electrical efficiency [4,5]. The execution of efficient electrocatalysts can decrease the over potentials ensuing the whole process less energy-intensive [2].

On the other hand, the depletion of fossil fuels and environmental change has obliged us to develop an alternative energy storage device which can provide high energy density corresponding to a large power density [6–8]. Supercapacitors provide higher energy density as compared to the conventional dielectric capacitors and large power density than that of the batteries [9,10]. In addition, fast charge–discharge (CD) rate and long cyclic stability of supercapacitor suggests its convenient service in electrical vehicles, flexible and portable electronics [10–12]. Current research approaches of supercapacitor emphasis on the enhancement of specific capacitance of the electrode materials as well as extending the potential window due to its quadratic relationship with the energy density [13,14]. Development of different positive and negative electrode materials along with proper charge or mass balancing can provides wide potential window as well as high specific capacitance [15,16]. Therefore, two different electroactive materials can be assembled to fabricate an asymmetric device to generate both pseudocapacitance and pure

---

[*] Corresponding author at: Surface Engineering and Tribology Division, CSIR-Central Mechanical Engineering Research Institute, Durgapur 713209, India.
E-mail addresses: tkuila@gmail.com, kuila@cmeri.res.in (T. Kuila).

http://dx.doi.org/10.1016/j.est.2016.02.007
2352-152X/

electrochemical double layer (EDL) capacitance during the CD process [17–20].

The paucity and cost limits the large scale application of platinum (Pt) which is the state-of-art of HER catalyst [2,5]. Alkaline water splitting has already established industrial applications for mass production of hydrogen. Ni and stainless steel are mostly used materials in industry for water splitting catalysis in basic solutions [5]. However, the high over potential and large Tafel slope restricts its application in HER. Therefore, the development of bifunctional HER catalysts in basic electrolytes is highly needed to overcome these limitations [2]. However, only a few reports are available in the literature on Ni-based hetero-structure (e.g., NiMo, NiFe LDH, Ni_2P and NiSe) for HER catalyst [2]. The use of hetero structure catalyst is advantageous as these promote fast electron transport during the catalytic process due to the generation of active sites and increased electrical conductivity [2,4,5]. The presence of NiO in the hetero structure possesses strong electrostatic affinity to the positively charged Ni^{2+} species due to the unfilled *d* orbital [5]. On the other hand, the transition metal oxide exhibits rich electrochemical activity with rapid and reversible surface or near-surface redox reactions [6]. Several advantages like low cost, good redox activity and high theoretical specific capacitance (1232 F g^{-1}) of MnO_2 make it very attractive as electrode materials [6,21,22]. It shows fast CD capability corresponding to the non-faradaic energy storage behaviour due to the adsorption of electrolyte ions on the surface along with the incorporation of protons [6,11]. Furthermore, the nano-sized NiO has very large theoretical capacitance (2584 F g^{-1}) and rich pseudocapacitive behaviour [23]. Multi-metal compound can be formed with MnO_2 and NiO to achieve superior electrochemical performance. Incorporation of metal ions within a different metal oxide introduces abundant structural defects in the multi-metal compounds [24]. In addition, hetero structure of different metal oxides create energy barrier so that a facile and short diffusion path for the ion or electron can be generated [25–27]. As a result, fast redox reactions as well as enhanced rate capability of the positive electrode material can be expected [24]. Supercapacitor performance of metal oxide like MnO_2 can further be improved by developing the nanostructure on the highly conductive substrates such as nano-structured oxides of different metal [28,29].

Herein, a simple *in-situ* hydrothermal technique to prepare MnO_2/NiO@Ni composite using Ni foam as the substrate has been reported. The developed multi-metal oxides coated Ni-foam was directly used as the HER and supercapacitor electrode. The developed MnO_2/NiO@Ni electrode shows high HER catalytic activity close to commercial Pt/C catalysts in aqueous KOH solution. In addition, the asymmetric supercapacitor (ASC) cell was designed with the MnO_2/NiO@Ni where thermally reduced graphene oxide (TRG) was used as the negative electrode material. GO can be reduced through different soft chemical and hydrothermal method which involves the use of various hazardous reducing agent. Further, only partial reduction is expected by these soft chemical methods. Therefore, GO has been reduced through heat treatment under inert gas atmosphere and formation of a few-layer TRG is expected. The ASC ensures its capability in high energy applications along with long life stability due to the synergistic effect of EDLC of negative electrode and rich pseudocapacitance of the positive electrode.

2. Experimental

2.1. Materials

Natural flake graphite was purchased from Sigma–Aldrich. Sulphuric acid, hydrogen peroxide, potassium permanganate and *N*,*N*-dimethyle formamide (DMF) were obtained from Merck, Mumbai, India. Conducting carbon black (EC-600JD, purity: >95%) and PVDF were purchased from MTI Corporation, USA. Ni-foam was purchased from Shanghai Winfay New Material Co., Ltd., China.

2.2. Preparation of MnO_2/NiO@Ni and TRG

Three pieces of Ni-foam (3 cm × 2 cm) was washed thoroughly with HCl solution and de-ionized (DI) water. $KMnO_4$ powder was dissolved in ~80 ml of DI water and poured in to a teflon lined autoclave. The weight ratio of the Ni-foam and $KMnO_4$ powder was 1:3. The autoclave was kept at 150 °C for ~20 h. The Ni-foams were collected and washed with DI water by vacuum filtration method to remove the excess $KMnO_4$. For the preparation of TRG, GO was prepared by modified Hummer's method as described earlier [17]. About 100 mg of freeze dried GO was taken in an alumina crucible and kept at 500 °C under argon atmosphere for 15 min inside a muffle furnace.

2.3. Structural and morphological characterization

The sample preparation for different characterization and property analysis of the electrode material has been described in the Supporting information. X-ray diffraction (XRD) studies of the composite were carried out at room temperature on a D/Max 2500 V/PC (Rigaku Corporation, Tokyo, Japan) at a scan rate of $1^\circ\,min^{-1}$ (Cu Kα radiation, $\lambda = 0.1542$ nm). The crystalline size of the nanoparticles was calculated for the peak line width using the Scherrer equation, $D = 0.9\lambda/B\cos\theta$, where, D is the dimension of the nanoparticles, λ is the wavelength of the $K\alpha$ radiation, B is the 'full width at half maximum' of the XRD peak, and θ is the corresponding angle [30–32]. Fourier transform infrared spectra (FT-IR) of pure TRG and MnO_2/NiO composite were obtained using a Nicolet iS10 instrument, Thermo Scientific, USA. The morphology of the MnO_2/NiO@Ni was measured by field emission scanning electron microscopy (FE-SEM) using Σigma HD, Carl Zeiss, Germany and transmission electron microscopy (TEM) was carried out using a JEM 2100 instrument (JEOL, Japan) at 200 kV. Raman spectra were recorded with Horiba Jobin Yvon (Kyoto, Japan).

2.4. Optical, electrical and electrochemical properties

The UV–vis spectroscopy was measured by Agilent Cary 60 spectrophotometer. Band gap was calculated according to the Tauc relationship:$\alpha h\nu = B(h\nu - E_g)^n$, where, α is the absorption coefficient, $h\nu$ is the energy of photon, B is a proportionality constant, E_g represents the optical band gap, and n is the parameter of specific electronic transition within the band due to the light absorption ($n = 1/2$, 2 for direct or indirect transition respectively) [33,34].

The electrical conductivity (σ) was measured using a four probe set up with a KEITHLEY delta system consisting of an AC and DC current source (model: 6221) and a Nanovoltmeter (model: 2182A) following the formula: $\sigma = 1/\rho = 1/4.532 \times R \times d$, where, ρ,R and d are the resistivity of the material, resistance and thickness of the prepared pellet [35,32]. The high and low current ranges during the measurement were recorded in the range of 20×10^{-6} to -20×10^{-6} A, and the delta voltage step was fixed at 100 mV s^{-1} for all the samples.

The electrochemical properties were analysed with PARSTAT 4000 (Princeton Applied Research, USA) electrochemical workstation using MnO_2/NiO@Ni as the working electrode. The HER properties were measured in KOH electrolyte and the measured potential (with respect to Ag/AgCl) was scaled to the reversible