

NiO-C NANOCOMPOSITE AND SUPERCAPACITOR APPLICATIONS

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Introduction

Supercapacitor is a novel energy storage device discovered by Beckers in 1957 [1]. They possess significantly higher energy storage compared to conventional capacitors while maintaining a high specific power, and are useful in bridging the energy-power gap between batteries and conventional capacitors. Some of the existing supercapacitor applications include load leveling, acceleration, emergency power, and braking energy recovery [3].

Nickel oxide (NiO) is a cheap transition metal oxide, which can form mesoporous structure with high surface area [2]. Coupled by its ability to utilize nano-dimension electrochemical double layer mechanism, as well as exhibiting pseudo-capacitance through Faradic redox reaction, NiO seems to be an excellent material for supercapacitors. Since the conductance of NiO is low, nano-composite of NiO-C was employed. In this paper, we report the properties of NiO and NiO-C nanocomposite, prepared using the chemical bath deposition (CBD) process.

Experimental

Materials

All the chemicals were of analytical grade and used without further purification. Hexa-hydrus nickel sulphate (1M NiSO₄·6H₂O), potassium persulphate (0.25M K₂S₂O₈) and aqueous ammonia (0.3M NH₄OH) were prepared separately under magnetic stirring. The prepared chemical solutions were then mixed in 4:3:1 volume ratio and left overnight for CBD growth under magnetic stirring. The deposited precursor powder was further purified using ethanol and water in a dissolution-centrifugation-decantation process.

The purified precursor powder was annealed at different temperatures (150°C, 200°C, 250°C, 300°C, 350°C, 400°C, 450°C, 500°C) at a ramp rate of 5°C/min and a dwell time of two hours.

The annealed NiO powder was mixed with commercial activated carbon and 5% polyvinylidene fluoride – methylpyrrolidene (PVDF-NMP) binder, to obtain the electrode material for coating on platinum-coated glass electrode substrates. 10%, 25%, 40%, 55% and 70% carbon mass compositions were chosen for electrode preparation. Finally, the electrodes were heated at 120°C for 30 minutes to vaporize the binder solvent.

Apparatus and Procedures

The electrochemical measurement of current-voltage (IV) relation was carried out using Autolab PGSTAT302N electrochemical station. Measurements

were taken over a potential range from zero to 500mV at scan rates of 100mVs⁻¹, 25mVs⁻¹ and 5mVs⁻¹. Platinum (Pt) counter electrode, saturated calomel reference electrode (SCE) at +0.242V, and 1M potassium hydroxide (KOH) electrolyte were used.

The electrodes were sputtered (BAL-TEC SCD 005) with 10nm of gold thin film to improve conductance and prevent charge building up, before characterization using field emission scanning electron microscopy (FESEM, Philips XL30 FEG).

Results and Discussion

The annealed NiO powder prepared was black in color. Figure 1 shows the typical redox behavior of the electrode. Against the SCE reference electrode, anodic and cathodic peaks were observed at around 0.39V and 0.23V respectively. The presence of redox peaks indicates the occurrence of Faradic redox reaction, which is contributed to the pseudo-capacitance behavior in NiO supercapacitor. In addition, the calculated specific capacitance decreased with an increase in scan rate.

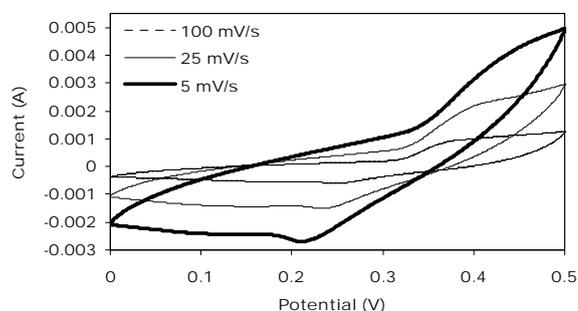


Fig. 1 Current-potential curve for NiO annealed at 500°C with 10%C

Figure 2 shows the relation between the specific capacitance against annealing temperature at a scan rate of 5mVs⁻¹, for NiO annealed at 500°C with 10%C. The specific capacitance is relatively stable below 200°C, and increases steadily to a maximum of 130.5Fg⁻¹ at 300°C. This increase is attributed to the increase of the specific surface area of NiO with annealing temperature. At a higher temperature, the specific capacitance was observed to taper off which may be due to decrease in conductance of NiO-C nanocomposite, since the C can be oxidized at the present nano-NiO.

The differential profile of Figure 2 is similar to the curve of the specific surface area against annealing temperature as reported by Cheng et. al. [2], indicating the importance of surface area on supercapacitor

performance. Two surface related phenomena were present, namely electrochemical double layer and Faradic redox reaction.

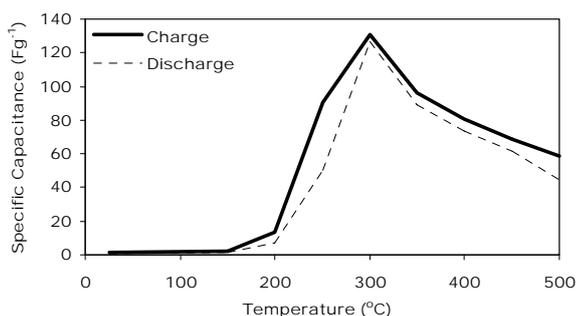


Fig. 2 Specific capacitance against annealing temperature for NiO annealed with 10%C

Figure 3 shows the relative specific capacitance $(C - C_0)/C_0$, where C is the specific capacitance of NiO-C composite and C_0 is from NiO, against carbon mass composition at a scan rate of 5mVs^{-1} , for NiO annealed at 300°C . An increase in specific capacitance for NiO with 10%C to 40%C is attributed to the increase in carbon-aided conductance. The maximum specific capacitance was achieved by 40%C, which remained relatively stable thereafter. This behavior may be due to the configuration of carbon around and within the NiO nanostructure, which was examined under FESEM.

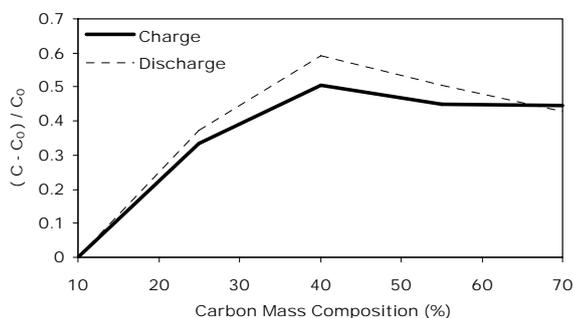


Fig. 3 Specific capacitance against mass composition of carbon for electrodes annealed at 300°C

Figure 4 shows the FESEM images of (a) NiO annealed at 300°C and (b) NiO-C nanocomposite annealed at 300°C with 40%C. The microstructure of NiO can be described as clusters of flower-like particles with radius of approximately $2.5\mu\text{m}$. Nano-leaves of approximately 400nm sheet length and 20nm thickness appeared in the flower-like morphology. The NiO FESEM image (Figure 4a) shows excellent porosity of mesoporous dimension. NiO annealed at other temperatures were observed to possess similar microstructure, despite variations in specific surface area as described earlier. This indicates that the variation in specific surface area was dominated by micropore variation during annealing, rather than mesopore structure. The NiO-C nanocomposite FESEM image (Figure 4b) shows significant agglomeration of activated carbon of

approximately 100nm radius. In addition, only the clusters that were smaller than the NiO micropore exhibited penetration into the NiO flower-like microstructure effectively.

The larger carbon clusters formed a shell layer around the NiO, which was completely surrounded at carbon composition of 40%C and above. This explains the earlier specific capacitance result that shows a relatively stable specific capacitance above 40%C, as there was no further increase in carbon-aided conductance. In addition, a thick carbon shell layer may even hinder electrolyte penetration onto the NiO surface, which explains the slight decrease in specific capacitance for NiO-C nanocomposites with high carbon mass composition.

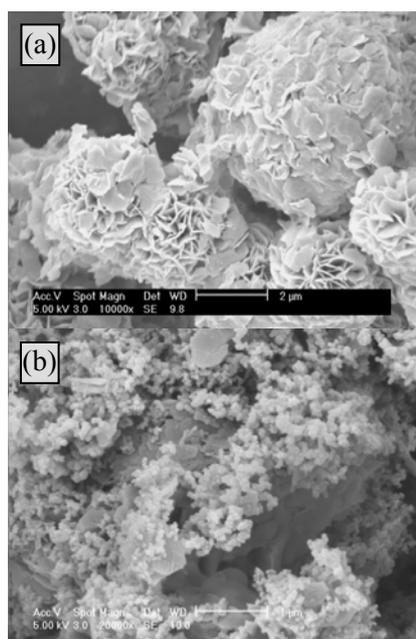


Fig. 4 FESEM images of (a) NiO annealed at 300°C and (b) NiO-C annealed at 300°C with 40%C

Conclusion

The properties of NiO and NiO-C nanocomposite, prepared using the chemical bath deposition (CBD) process were investigated. The maximum specific capacitance achieved was 130.5Fg^{-1} at a scan rate of 5mVs^{-1} . For the NiO-C nanocomposites, maximum specific capacitance was achieved at 40%C, and remained constant with further increase in carbon mass composition. FESEM results revealed that the activated carbon agglomerates to form clusters, and the larger clusters form a shell layer around the NiO microstructure, leading to a decrease in the specific capacitance of charge.

References

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2. J. Cheng, G.P. Cao, Y.S. Yang, et. al. (2006) Journal of Power Sources, 159, 734-741
3. R. Kotz, M. Carlen (2000) Electrochimica Acta, 45, 2483-2498