Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 105 (2017) 4848 – 4853

Energy Procedia

The 8th International Conference on Applied Energy – ICAE2016

Hierarchical grass like $NiCo_2O_4$ nanoflakes on 3-dimensional microporous electrically conductive network with Superior Electrochemical Performance

Mai Li[a], Yuanhao Wang[b], Dajun Wu[c], Lianwei Wang[c] and Hongxing Yang[a*]

[a]*Renewable Energy Research Group, Department of Building Services Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China*

[b]*Faculty of Science and Technology, Technological and Higher Education Institute of Hong Kong, New Territories, Hong Kong*

[c]*Key Laboratory of Polar Materials and Devices, Ministry of Education, and Department of Electronic Engineering, East China Normal University, 500 Dongchuan Road, Shanghai 200241, P. R. China*

Abstract

Bimetallic oxide nickel cobaltite ($NiCo_2O_4$) nanoflakes are fabricated on the surface and sidewall of three dimensional microporous electrically conductive network (MECN) as the active electrode materials for miniature supercapacitors by hydrothermal method. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) characterisation of as-prepared material demonstrates that the nanostructure grown on the MECN consists of a $NiCo_2O_4$ nanoflake layer. Compared with the nanostructured nickel growth on the MECN, the as-prepared $NiCo_2O_4$/MECN nanoflake has shown enhanced electrochemical properties, manifesting a high capacitance of 607.29 F g^{-1} (7.29 F cm^{-2}) at 10 mA cm^{-2} and good cycling stability of 60.60% capacity retention after 2000 cycles. Even at the power density of 1000.0 W Kg^{-1}, the device still has the energy density of 134.71 Wh Kg^{-1} which is comparable to related research. The large specific capacitance and remarkable rate capability can attribute to the unique 3D ordered porous architecture, which facilitates electron and ion transport, enlarges the liquid-solid interfacial area, and enhances the utilization efficiency of the active materials. Meanwhile, the weight and size of the device are reduced.

Peer-review under responsibility of the scientific committee of the 8th International Conference on Applied Energy.

Keywords: supercapacitors; microporous electrically conductive network; nickel cobaltite; energy storage; 3D structure

1. Introduction

With the technological and scientific advancements in the 21st century, our modern society is facing the energy and environmental related issues such as deficiency, pollution of fossil fuels and global warming[1]. To meet urgent needs for sustainable and renewable power sources in the modern electronic industry, many effort has been made in developing energy storage and conversion form clean and renewable energy sources [2, 3]. Electrochemical capacitors (ECs), that store energy using both ion adsorption-desorption and electrochemical reaction, have attracted much attention for their high power

Peer-review under responsibility of the scientific committee of the 8th International Conference on Applied Energy.
doi:10.1016/j.egypro.2017.03.960

density, long lifespan and charge/discharge efficiency application. With characteristics complementary to those of rechargeable batteries and fuel cell, supercapacitors have been used in many application, such as power back-up, pacemakers, air bags and electrical vehicles [4, 5]. Therefore, much effort has been put into exploring new ways of manufacturing high performance supercapacitors which can deliver high power within a very short time and store a large amount of energy.

Recently, mixed metal oxides and binary metal oxides have been reported to show higher performance than single component oxides due to their feasible oxidation states and high electrical conductivity, such as $ZnCo_2O_4$,[6] Zn_2SnO_4,[7] $NiMoO_4$,[8] $CoMoO_4$ [9] and $NiCo_2O_4$ [1, 10] et, al. seems to be the most promising materials for ECs. Among those materials, $NiCo_2O_4$ is advantageous because it is low cost, non-toxic, and exhibits enhanced electrochemical properties. Due to its excellent nano morphology structure (Fig.1 (e)-(h)) and stable electrochemical properties, $NiCo_2O_4$ has become a hot research topic in the near few years. So far, the main synthesis strategies include liquid-phase co-precipitation,[11] hydro- and solvothermal routes, [12] microwave-assisted methods,[13] electrodeposition methods,[14] electrospinning methods,[15] high-temperture synthesis[16] etc. Actually, most of the methods are suitable for the growth of active material on large aperture porous or 2 dimension planar electrodes but do not suitable for the growth of active substances in the internal channels of MECN. Therefore, among those methods, in comparison, the hydrothermal synthesis route has several advantages for nanomaterials growth in the MECN. First of all, instead of producing the active materials in a complex environment, the materials can be deposited directly on a substrate and so the microstructure of the active materials can be preserved. Secondly, the active materials can be deposited directly without the need of adding a polymer binder and conduction agent, and so the conductivity and purity of the active materials will not be affected by additives. Thirdly, the reaction carried out in the high temperature and pressure environment, the reaction solution can easily penetrate into the inside of the nanoscale electrode substrate, so that the hierarchical $NiCo_2O_4$ nano-sturcture growth uniform on both the surface and side wall of MECN[9]. The fabrication process of MECN can be find from literature by Mai Li etc.[9] and the synthetic methods of $NiCo_2O_4$ can be find from the literature by Suning Gao etc.[10].

2. The structure of nanoscale covered MECN and the $NiCo_2O_4$/MECN composite structure

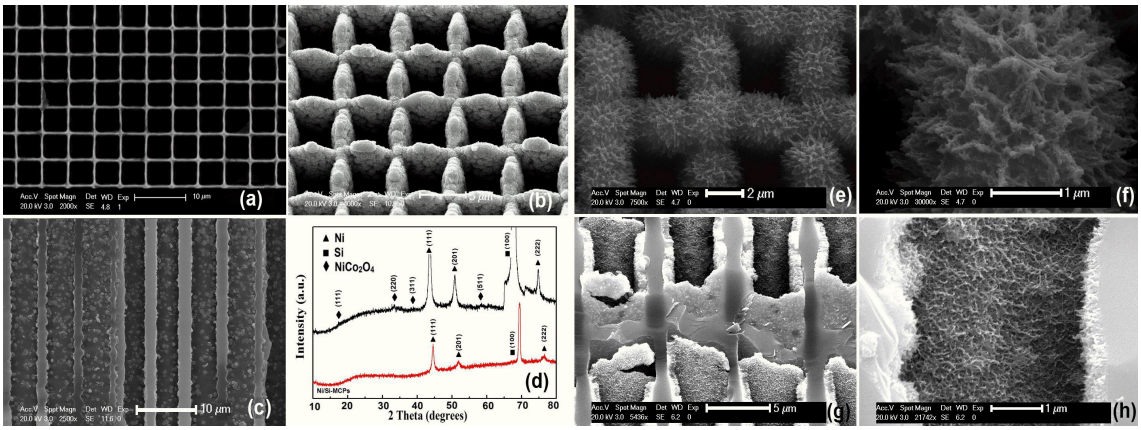

Fig.1. (a) the surface of silicon micro channel plate (Si-MCP), (b) the surface of microporous electrically conductive network (MECN), (c) the morphology of nickel growth on the surface of MECN, (d) the XRD patterns of MECN and $NiCo_2O_4$/MECN, (e) the surface of $NiCo_2O_4$/MECN electrode, (f) the nanoflake structure of $NiCo_2O_4$, (g) the cross-sectional view, (h) magnified image of (g).

It is well known that the pseudocapacitance is mainly produced by fast faradic reactions associated with double injection (extraction) of ions and electrons[9]. To improve supercapacitive behavior, it is

crucial to enhance the kinetics of ion and electron transport inside the electrodes and at the electrode/electrolyte interface. Porous three-dimensional (3D) silicon micro channel plate (Si-MCP) act as skeleton substrate, enabling access of ions and electrons to the active surfaces and produce a better electrochemical response on the electrodes. After the fabrication of Si-MCP by silicon process, a nickel layer was grown on the surface of Si-MCP as the conductive layer of the electrode that formation the MECN as shown in Fig.1 (a)-(c). In this work, we report a novel strategy to prepare ordered hierarchical $NiCo_2O_4$ films via hydrothermal synthesis route based on microporous electrically conductive network (MECN) with a large aspect ratio for the production of novel supercapacitors. The inner channels of the MECN provide all the space needed for the nickel current collector layer and $NiCo_2O_4$ active materials in the supercapacitors. So the footprint of the whole electrode can be reduced while maintaining the advantage of a large surface area for the active materials due to the nano-crystals on the inner walls of the microchannels. Fig. 1 shows the large specific surface area design concept and unit structure of our miniature supercapacitors which vividly reveals the advantages of MECN.

Fig.1. (e)-(h) show the morphology of the bimetallic oxide nickel cobaltite thin film on the MECN as observed by field-emission scanning electron microscopy (FE-SEM) at different magnifications. As shown in Fig. 1(e), the sandwich-like MECN with a large surface area provide more $NiCo_2O_4$ nucleation centers and also good support with high conductivity to decrease the contact resistance of the active materials. After hydrothermal synthesis, a smooth and compact $NiCo_2O_4$ layer about 300 nm thick is formed and cracks between the active materials resulting from deposition can be observed in Fig. 1(f) and (g). The nano-flakes on the top walls in Fig. 1(f) are larger than those on the sidewalls shown in Fig. 1(g). According to the cross-sectional SEM morphology of the $NiCo_2O_4$/MECN in Fig. 1(g), $NiCo_2O_4$ is deposited uniformly onto the sidewalls of the microchannel and this is favorable to enhanced performance. In order to determine the structure and crystallinity of the samples, XRD measurements were employed to record the patterns with the MECN and $NiCo_2O_4$/MECN. Fig. 1(d) absolutely exhibits the peaks that belonged to spinel $NiCo_2O_4$ (JCPDS data no.73-1702) and the XRD pattern of the bare MECN substrate is shown in this picture[10].

3. Electrochemical performance of the $NiCo_2O_4$/MECN electrode

Cyclic voltammogram (CV) and chronopotentiometry measurements are conducted to evaluate the specific capacitance and electrochemical properties of the as-prepared $NiCo_2O_4$/MECN electrodes. Fig. 3(a)–(c) show the CV curves of the MECN and $NiCo_2O_4$/MECN electrode in 2 M KOH at various sweeping rates in the potential range between -0.2 and 0.6 V. As shown in Fig. 2(a), as the scanning rate goes up, the peak currents are proportional to the square root of the scanning rates, implying that the electrodes have good electrochemical performance. In the reverse scanning direction, the current is almost instantaneous suggesting that in the CV curve, there is a small angle along the horizontal axis, indicating that the barely MECN electrodes have smaller impedance. The CV of the MECN normally approaches the ideal shape of redox reaction, but the CV obtained from the $NiCo_2O_4$/MECN pseudo-capacitance is quite different. While, Furthermore, it is apparent from Fig.2 (b) that $NiCo_2O_4$/MECN possesses a much larger area under the same current-potential compared to nano nickel covered MECN suggesting that $NiCo_2O_4$ has an excellent electrochemical performance based on the MECN and the capacitance of MECN can be ignored (Fig. 3 (c)). The structure of the $NiCo_2O_4$ nano-flakes provides reaction sites due to the huge surface area and porous structure of the MECN. While the CV of $NiCo_2O_4$/MECN under large scanning rate have large angle along the horizontal axis that indicate us the chemical reaction of $NiCo_2O_4$ is not sufficient under this situation. The specific capacitance can be calculated from the CV curves using Eq. (1):[17]

$$C_f = (\int i dt)(A\Delta V)^{-1} \quad (1)$$

where C_f is the electrode specific capacitance, i is the instantaneous current, A is the footprint area of the entire electrode, and ΔV is potential voltage window. The specific capacitance can be calculated from the CV curves. Fig. 2(d) displays the charge-discharge curves of the as-prepared $NiCo_2O_4$/MECN

electrode measured in 2 M KOH at different discharge current densities in the potential range from 0 to 0.4 V. According to the shape of the charge-discharge curves, it is mainly pseudo-capacitance instead of pure double-layer capacitance and the results are consistent with the CV data of Fig. 2(b). Chronopotentiometry is a recommended method to determine the capacitance of supercapacitors according to eqn (2): [17]

$$C_f = (I\Delta t)(A\Delta E)^{-1} \quad (2)$$

where I is the constant discharge current, Δt is the discharge time, ΔE is the potential drop during the discharge process and A is the area of the working electrode immersed in KOH.

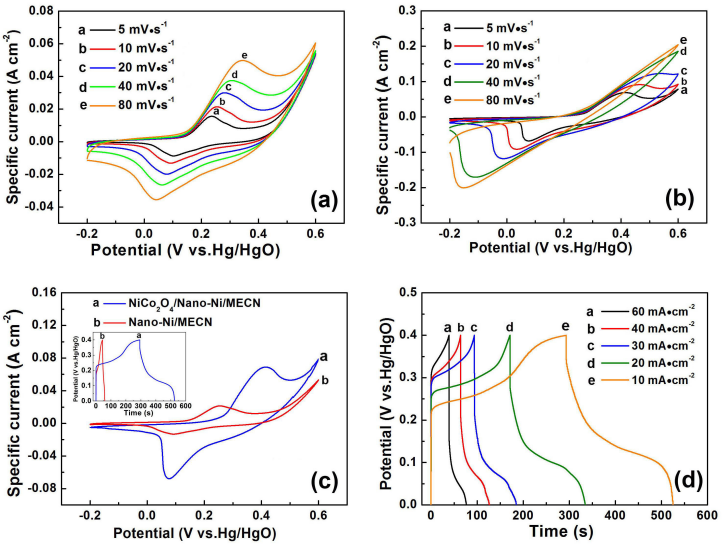

Fig.2. (a) CV curves of MECN and (b) CV curves of $NiCo_2O_4$/MECN under different scanning rate, (c) the CV and chronopotentiometry comparison between the MECN and $NiCo_2O_4$/MECN, (d) the chronopotentiometry of $NiCo_2O_4$/MECN under different current density.

According to the chronopotentiometry, as shown in Fig. 3(a), the area capacity values of $NiCo_2O_4$/MECN are calculated to be 7.29, 7.04, 6.78, 6.27 and 5.63 F cm^{-2} for discharging current densities of 10, 20, 30, 40 and 60 mA cm^{-2}, respectively. Due to the mass of the $NiCo_2O_4$ is 0.012g on the sample, the mass capacity values of $NiCo_2O_4$/MECN are calculated to be 607.29, 586.33, 565.08, 522.67 and 467.75 F g^{-1} for discharging current densities of 10, 20, 30, 40 and 60 mA cm^{-2}, respectively.

It indicates the excellent ability of the supercapacitors. The energy and power densities (E and P) are calculated using the following equ(3) and (4):[18]

$$E = \frac{0.5C(\Delta V)^2}{3.6} \quad (3)$$

$$P = \frac{E \times 3600}{\Delta t} \quad (4)$$

where C is specific capacitance, ΔV is the potential window, Δt is the discharge time. As shown in Fig. 3(b), the supercapacitor displays a high energy density of 174.90 Wh kg^{-1} at a power density of 208.30W kg^{-1}. Even at a high power density of 1000.0 W kg^{-1}, the device still has an energy density of 134.71 Wh kg^{-1} that is much better than that of the conventional EDLC.

In order to demonstrate the long term electrochemical stability of the nano-flaked $NiCo_2O_4$ electrode materials, the IT characteristics were measured in 2 M KOH at a current density 70 mA cm^{-2}. As shown in Fig. 3(c), the specific capacitance calculated from eqn (2) decreases with cycle numbers. In the first 1000 cycles, the calculated capacitance loss of $NiCo_2O_4$ was 27.6%, while in the last 1000 cycles, the

sample have capacitance loss of 11.8%, thereby demonstrating good stability in long charging–discharging cycles. It has been proposed that a smaller surface area and degradation of the active materials are responsible for the capacitance loss in long charging–discharging. Another important aspect of a supercapacitor electrode is the impedance spectra. The measurements were carried out on the $NiCo_2O_4$/MECN electrodes with an excitation signal of 5 mV for those samples. The EIS of the MECN and $NiCo_2O_4$/MECN before and after cycling tests (Fig.3 (d)) are also consistent with the other electrochemical tests that exaggerate the excellent performance of the $NiCo_2O_4$. The MECN has a fast reaction rate and contact resistance with the electrolyte, while the $NiCo_2O_4$/MECN has much more has more active materials that can react violent with the electrolyte. From EIS, we also find that after 2000 cycles under large current density, the active materials of $NiCo_2O_4$/MECN reduced dramatically but the ion migration ability enhanced that may due to the reaction changed the composition of the substance.[5]

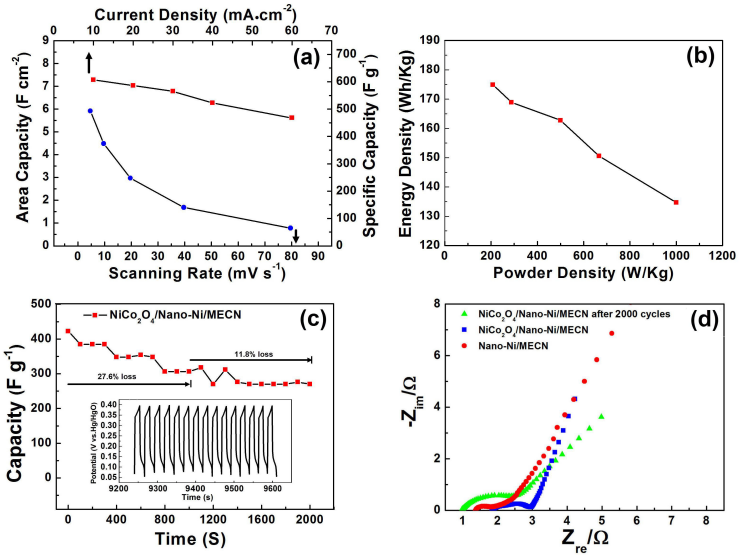

Fig.3. (a) the capacity of $NiCo_2O_4$/MECN under different calculation methods, (b) Ragone plot of the $NiCo_2O_4$/MECN under different current density, (c) 2000 cycles cycling ability test of the $NiCo_2O_4$/MECN, (d) the EIS plot of the samples of MECN and $NiCo_2O_4$/MECN before and after the 2000 cycling ability test.

4. Conclusions

The effects, mechanism, electrochemical performance of an improved bimetallic oxide nickel cobaltite coated MECN fabricated by hydrothermal method are investigated. The structure with the nanoflake $NiCo_2O_4$ film exhibits much higher specific capacitance than the barely MECN. This can be attributed to the regular nano-structure consisting of mesopores and faster redox reaction of $NiCo_2O_4$. The highest specific capacitance of 7.29 F cm^{-2} (607.29 F g^{-1}) was attained at a discharge current density of 10 mA cm^{-2} and there is good electrochemical stability up to 2000 cycles. The materials can be readily upscaled to mass production of miniature supercapacitors.

Acknowledgements

This project is financially supported by the Construction Industry Council and The Hong Kong Polytechnic University. Appreciations are also given to the Key Laboratory of Polar Materials and Devices, Ministry of Education, and Department of Electronic Engineering, East China Normal University for doing the experiments.

References

[1] D.P. Dubal, P. Gomez-Romero, B.R. Sankapal, R. Holze, Nickel cobaltite as an emerging material for supercapacitors: An overview, Nano Energy, 11 (2015) 377-399.
[2] R. Sharma, C.C.B. Bufon, D. Grimm, R. Sommer, A. Wollatz, J. Schadewald, D.J. Thurmer, P.F. Siles, M. Bauer, O.G. Schmidt, Large-Area Rolled-Up Nanomembrane Capacitor Arrays for Electrostatic Energy Storage, Advanced Energy Materials, 4 (2014) 1301631.
[3] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, Nature materials, 7 (2008) 845-854.
[4] A. Burke, Ultracapacitors: why, how, and where is the technology, Journal of Power Sources, 91 (2000) 37-50.
[5] M. Li, S. Xu, T. Liu, F. Wang, P. Yang, L. Wang, P.K. Chu, Electrochemically-deposited nanostructured $Co(OH)_2$ flakes on three-dimensional ordered nickel/silicon microchannel plates for miniature supercapacitors, Journal of Materials Chemistry A, 1 (2013) 532-540.
[6] K. Karthikeyan, D. Kalpana, N. Renganathan, Synthesis and characterization of $ZnCo_2O_4$ nanomaterial for symmetric supercapacitor applications, Ionics, 15 (2009) 107-110.
[7] L. Bao, J. Zang, X. Li, Flexible Zn_2SnO_4/MnO_2 Core/Shell Nanocable−Carbon Microfiber Hybrid Composites for High-Performance Supercapacitor Electrodes, Nano Letters, 11 (2011) 1215-1220.
[8] D. Cai, B. Liu, D. Wang, Y. Liu, L. Wang, H. Li, Y. Wang, C. Wang, Q. Li, T. Wang, Facile hydrothermal synthesis of hierarchical ultrathin mesoporous $NiMoO_4$ nanosheets for high performance supercapacitors, Electrochimica Acta, 115 (2014) 358-363.
[9] M. Li, S. Xu, C. Cherry, Y. Zhu, D. Wu, C. Zhang, X. Zhang, R. Huang, R. Qi, L. Wang, Hierarchical 3-dimensional $CoMoO_4$ nanoflakes on a macroporous electrically conductive network with superior electrochemical performance, Journal of Materials Chemistry A, 3 (2015) 13776-13785.
[10] S. Gao, F. Liao, S. Ma, L. Zhu, M. Shao, Network-like mesoporous $NiCo_2O_4$ grown on carbon cloth for high-performance pseudocapacitors, Journal of Materials Chemistry A, 3 (2015) 16520-16527.
[11] C. Yuan, J. Li, L. Hou, L. Yang, L. Shen, X. Zhang, Facile template-free synthesis of ultralayered mesoporous nickel cobaltite nanowires towards high-performance electrochemical capacitors, Journal of Materials Chemistry, 22 (2012) 16084-16090.
[12] Q. Wang, B. Liu, X. Wang, S. Ran, L. Wang, D. Chen, G. Shen, Morphology evolution of urchin-like $NiCo_2O_4$ nanostructures and their applications as psuedocapacitors and photoelectrochemical cells, Journal of Materials Chemistry, 22 (2012) 21647-21653.
[13] D. Carriazo, J. Patino, M.C. Gutierrez, M.L. Ferrer, F. del Monte, Microwave-assisted synthesis of $NiCo_2O_4$-graphene oxide nanocomposites suitable as electrodes for supercapacitors, RSC Advances, 3 (2013) 13690-13695.
[14] L. Qian, L. Gu, L. Yang, H. Yuan, D. Xiao, Direct growth of $NiCo_2O_4$ nanostructures on conductive substrates with enhanced electrocatalytic activity and stability for methanol oxidation, Nanoscale, 5 (2013) 7388-7396.
[15] M. Prabu, K. Ketpang, S. Shanmugam, Hierarchical nanostructured $NiCo_2O_4$ as an efficient bifunctional non-precious metal catalyst for rechargeable zinc-air batteries, Nanoscale, 6 (2014) 3173-3181.
[16] S. Verma, H.M. Joshi, T. Jagadale, A. Chawla, R. Chandra, S. Ogale, Nearly Monodispersed Multifunctional $NiCo_2O_4$ Spinel Nanoparticles: Magnetism, Infrared Transparency, and Radiofrequency Absorption, The Journal of Physical Chemistry C, 112 (2008) 15106-15112.
[17] E. Umeshbabu, G. Rajeshkhanna, P. Justin, G.R. Rao, Synthesis of mesoporous $NiCo_2O_4$-rGO by a solvothermal method for charge storage applications, RSC Advances, 5 (2015) 66657-66666.
[18] M. Li, S. Xu, C. Cherry, Y. Zhu, R. Huang, R. Qi, P. Yang, L. Wang, P.K. Chu, Asymmetrical Supercapacitor Composed of Thin $Co(OH)_2$ Nanoflakes on Three-Dimensional Ni/Si Microchannel Plates with Superior Electrochemical Performance, Electrochimica Acta, 149 (2014) 18-27.