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Fabrication of Bimetallic Oxides (MCo_2O_4 : $\text{M}=\text{Cu}, \text{Mn}$) on Ordered Microchannel Electro-Conductive Plate for High-Performance Hybrid Supercapacitors

Mai Li ^{1,*}, Zheyi Meng ^{2,*}, Ruichao Feng ³, Kailan Zhu ¹, Fengfeng Zhao ³, Chunrui Wang ¹, Jiale Wang ¹, Lianwei Wang ⁴ and Paul K. Chu ^{5,6,7} 

- ¹ College of Science, Donghua University, Shanghai 201620, China; zhukl1029@163.com (K.Z.); crwang@dhu.edu.cn (C.W.); jiale.wang@dhu.edu.cn (J.W.)
 - ² State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science, Donghua University, Shanghai 201620, China
 - ³ College of Mathematics and Physics, Shanghai University of Electric Power, Shanghai 200090, China; frcdex@163.com (R.F.); zhaoff0425@163.com (F.Z.)
 - ⁴ Key Laboratory of Polar Materials and Devices (MOE), Department of Electronics, East China Normal University, Shanghai 200241, China; wang_lw@hotmail.com
 - ⁵ Department of Physics, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China; paul.chu@cityu.edu.hk
 - ⁶ Department of Materials Science and Engineering, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China
 - ⁷ Department of Biomedical Engineering, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China
- * Correspondence: limai@dhu.edu.cn (M.L.); mengzheyi@dhu.edu.cn (Z.M.)



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Abstract: AB_2O_4 -type binary-transition metal oxides (BTMOs) of CuCo_2O_4 and MnCo_2O_4 were successfully prepared on ordered macroporous electrode plates (OMEP) for supercapacitors. Under the current density of 5 mA cm^{-2} , the CuCo_2O_4 /OMEP electrode achieved a specific capacitance of 1199 F g^{-1} . The asymmetric supercapacitor device prepared using CuCo_2O_4 /OMEP as the positive electrode and carbon-based materials as the negative electrode (CuCo_2O_4 /OMEP//AC) achieved the power density of 14.58 kW kg^{-1} under the energy density of 11.7 Wh kg^{-1} . After 10,000 GCD cycles, the loss capacitance of CuCo_2O_4 /OMEP//AC is only 7.5% (the retention is 92.5%). The MnCo_2O_4 /OMEP electrode shows the specific and area capacitance of 843 F g^{-1} and 5.39 F cm^{-2} at 5 mA cm^{-2} . The MnCo_2O_4 /OMEP-based supercapacitor device (MnCo_2O_4 /OMEP//AC) has a power density of 8.33 kW kg^{-1} under the energy density of 11.6 Wh kg^{-1} and the cycle stability was 90.2% after 10,000 cycles. The excellent power density and cycle stability prove that the prepared hybrid supercapacitor fabricated under silicon process has a good prospect as the power buffer device for solar cells.

Keywords: power buffer; silicon micromachining; bimetallic oxide; ordered macropore structure; electrochemical; supercapacitor

1. Introduction

Currently, with the continuous expansion of energy demand, as an important device to stabilize energy input and output, the research on energy storage components has become more and more the focus of future sustainable development [1]. After the solar cell generates electric energy, storing this energy through the energy storage system integrated with microelectronic technology to fulfill the stable and safe utilization of energy remains a challenge for the efficient application of solar energy [2,3]. The complex environment of solar cell power generation and storage is pursuing the characteristics of high-power density, long lifecycle and low cost, which are consistent with the research concept of electrode materials for supercapacitors [4]. Binary transition metal oxides (BTMOs) are



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important multifunctional materials composed of two metal elements. Due to their unique structure and properties, they have attracted extensive attention in catalysis, heavy metal ion adsorption, electrocatalyst, sensor, lithium-ion batteries and supercapacitors [5–8]. Among those bimetallic oxides, cobalt-based AB_2O_4 BTMOS such as $CuCo_2O_4$, $ZnCo_2O_4$, $NiCo_2O_4$, $MnCo_2O_4$ and $FeCo_2O_4$ have attracted extensive attention due to their high specific capacitance, better rate performance and stability electrochemical properties, and are considered to have the most potential electrode material for energy storage, especially supercapacitors [9–13].

Cu, Mn, Fe and other metal atoms replace Co atoms in Co_3O_4 to form a MCo_2O_4 type bimetallic oxide, which increases the Faraday redox reaction site with a higher capacity and reduces the production cost of the active material without changing the spinel structure of Co_3O_4 [11,14,15]. However, the untreated bimetallic oxides have low conductivity and are easy to agglomerate during the reaction, which limits their further application in supercapacitors [16,17]. Selecting appropriate bimetallic oxides, and then advanced electrode structure design and nanomaterial preparation process, is an effective means to enhance the ion transport and structural stability of bimetallic oxides in the process of electrochemical reaction. Among those MCo_2O_4 type materials, $CuCo_2O_4$ and $MnCo_2O_4$ are two kinds of active materials with different electrical active elements, which have received extensive attention in recent years [16,18–20]. Zhang et al. [21] reported the specific capacitance of $CuCo_2O_4@CuCo_2O_4/Ni$ foam electrode up to 888.9 F g^{-1} at 2 mA cm^{-2} ; Pang et al. worked on $\delta\text{-MnO}_2$ -added $CuCo_2O_4$ which shows a maximum specific capacitance of 1180 F g^{-1} at 1 A g^{-1} and remains 93.2% after 5000 GCD cycles [22]. Lee's $MnCo_2O_4\text{-}NiCo_2O_4$ composite electrodes exhibit a high specific capacitance of 1152 F g^{-1} at 1 A g^{-1} , and excellent rate capability and superior cycling stability (95.38% retention after 3000 cycles) [23]. These studies showed that the cobalt-based bimetallic oxide has a good application prospect for energy storage equipment.

Here, MCo_2O_4 ($M=Cu, Mn$) nanosheets were prepared on a three-dimensional ordered macroporous electrode plate (OMEP) through the hydrothermal method as high-performance multi-dimensional Faraday electrodes [24]. Although there are many studies on porous materials in the field of energy storage in recent years, there is little similar research on ordered porous materials such as OMEP, and the research materials combined with AB_2O_4 bimetallic oxides have just emerged [21]. OMEP, composed of millions of neatly arranged porous structures fabricated by the silicon micromachining process, acts as a conductive substrate in the multidimensional composite electrode to effectively prevent the agglomeration of nanomaterials [25,26]. A stable nickel coating on the OMEP surface not only can improve the electrical conductivity of the electrode, but it also acts as the nucleation center of the active material, allowing the active material to adhere tightly to the surface of the nickel layer, without the need for an additional conductive agent or polymer binder. Therefore, the electrodes prepared with OMEP can objectively reflect the performance characteristics of specific active substances.

In this paper, $CuCo_2O_4$ /OMEP electrodes and $MnCo_2O_4$ /OMEP electrodes were successfully prepared by using nickel-plated ordered macroporous electrode-conductive plates (OMEP) as the substrate. These composite electrodes have a unique three-dimensional porous structure, which facilitates the transport of electrons and ions, increases the liquid-solid interface area, improves the utilization efficiency of the active material and reduces the weight and size of the electrode, which makes the active material obtain a large specific capacitance for miniature supercapacitors [27]. The $MnCo_2O_4$ /OMEP electrode shows the specific and area capacitance of 843 F g^{-1} and 2.7 F cm^{-2} at 5 mA cm^{-2} . The $MnCo_2O_4$ /OMEP-based supercapacitor device ($MnCo_2O_4$ /OMEP//AC) has a power density of 8.33 kW kg^{-1} under the energy density of 11.6 Wh kg^{-1} and the cycle stability was 90.2% after 10,000 cycles. The $CuCo_2O_4$ /OMEP electrode has high cycle stability and maintains a good ratio at a higher current density and CV scanning speed. The specific capacitance of the electrode is 1199 F g^{-1} at the current density of 5 mA cm^{-2} . The asymmetric supercapacitors prepared using the $CuCo_2O_4$ /OMEP electrode and activated carbon

electrode ($\text{CuCo}_2\text{O}_4/\text{OMEF}/\text{AC}$) has obtained the power density of 14.58 kW kg^{-1} under the energy density of 11.7 Wh kg^{-1} . After 10,000 GCD cycles, the loss capacitance of $\text{CuCo}_2\text{O}_4/\text{OMEF}/\text{AC}$ is only 7.5%.

2. Materials and Methods

2.1. Preparation of OMEP

The silicon macroporous microchannel plate (Si-MCP, Figure 1a,b) is the skeleton structure of OMEP. Its fabrication process can be divided into three steps: pretreatment, deep etching and stripping. Pretreatment stage: select (100) crystal p-type silicon wafer, grow silica mask layer through thermal oxidation, define the hole pattern by lithography, use buffered oxide etchant (BOE) etching solution to expose the holes that need to be etched from the silica mask layer, remove the photoresist to obtain the desired pattern. The wafer is anisotropically etched in 25% tetramethylammonium hydroxide solution and stops etching when a distinct cross pattern is seen under the microscope. The pretreated silicon wafer was subjected to deep photochemical etching [28] and the peel steps are followed to obtain the required Si-MCP. A layer of nickel was uniformly deposited on the outer and inner surfaces of Si-MCP by liquid flow method [29–31] to fabricate the OMEP (Figure 1c–f). To further improve the electrical conductivity and specific surface area of the OMEP, the electroplating nickel method was carried out to deposition a nickel particle layer on OMEP after chemical deposition. At room temperature of $(23 \pm 1)^\circ\text{C}$, the electrolyte consisted of 2 M ammonium chloride and 0.1 M nickel chloride, and the pH was adjusted to 3.5. After nickel deposition, the morphologies of the surface and sidewalls at different magnification are shown in Figure 1c–f. It can be seen from the figure that a layer of nickel evenly covers the surface and sidewalls of the Si-MCP.

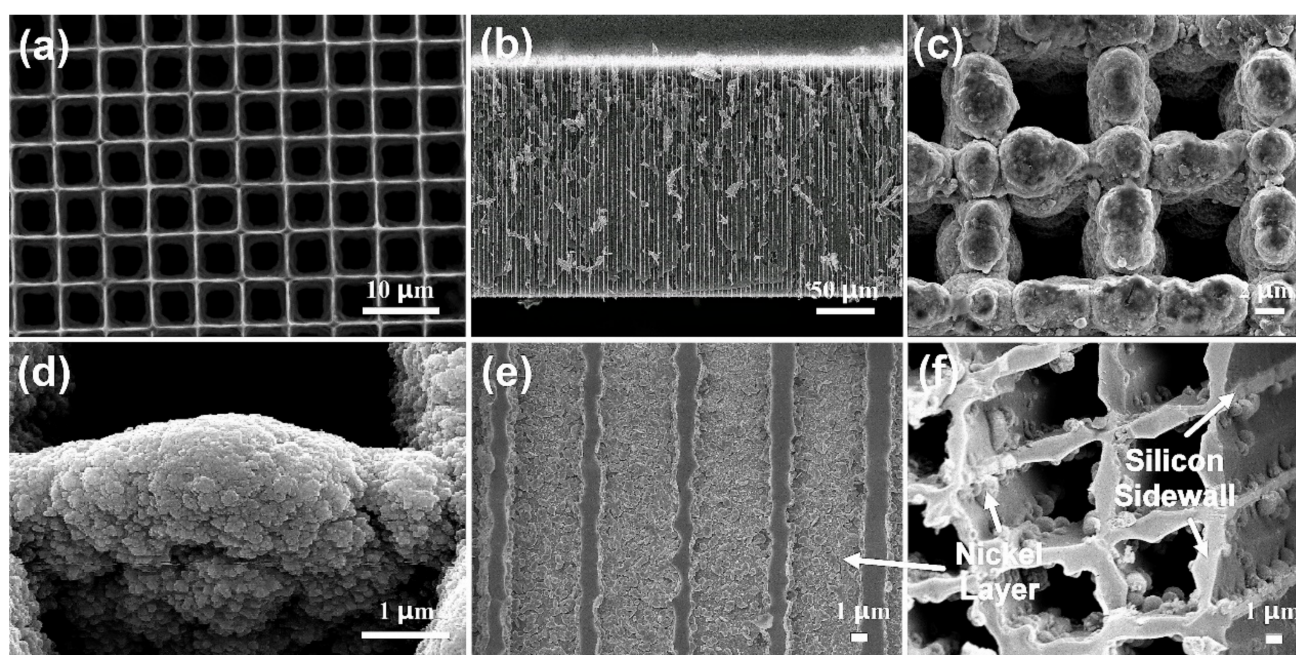


Figure 1. SEM images: (a) top surface of the ordered Si-MCP; (b) sidewall of Si-MCPs; (c,d) top surface of nano-Ni covered OMEP with different magnification; (e,f) sidewall of OMEP with different magnification.

2.2. Synthesis of the $\text{CuCo}_2\text{O}_4/\text{OMEF}$ and $\text{MnCo}_2\text{O}_4/\text{OMEF}$ Electrode

To fabricate the $\text{CuCo}_2\text{O}_4/\text{OMEF}$ electrode, a mixture of 1 mmol copper nitrate and 2 mmol cobalt nitrate was added with 15 mmol urea as precipitators. The solution was fully stirred and mixed and put into a reactor with OMEP in front of it. The hydrothermal reaction lasted for 8 h at 120°C and then cooled to room temperature naturally. The $\text{CuCo}_2\text{O}_4/\text{OMEF}$ electrode was prepared after the samples were rinsed and dried at 60°C .

for 24 h. The preparation method and steps of the $\text{MnCo}_2\text{O}_4/\text{OMEP}$ electrode are the same as the $\text{CuCo}_2\text{O}_4/\text{OMEP}$ electrode, but the difference is that the copper nitrate used in $\text{CuCo}_2\text{O}_4/\text{OMEP}$ fabrication is replaced by manganese sulfate in hydrothermal reaction. The procedure for preparing samples on the surface of nickel foam is consistent with that of OMEP-based samples, except that the substrate is changed from OMEP to nickel foam. At the same time, the CuCo_2O_4 and MnCo_2O_4 fabricated on nickel foam were named $\text{CuCo}_2\text{O}_4/\text{NF}$ and $\text{MnCo}_2\text{O}_4/\text{NF}$, respectively.

2.3. Characterization

Scanning electron microscopy (SEM, JEOLJSM-7001F, Tokyo, Japan) was used to study the morphology and microstructure of various electrodes. X-ray diffraction (XRD, Rigaku, RINT2000, Tokyo, Japan) was used to study the crystal structure and X-ray photoelectron spectroscopy (XPS, Kratons Axis Ultra DLD) was used to determine the elemental composition of the fabricated electrodes.

In this paper, CHI660E electrochemical workstation was used to perform performance tests in 2 M KOH electrolyte. OMEP, $\text{Co}_3\text{O}_4/\text{OMEP}$, $\text{CuCo}_2\text{O}_4/\text{NF}$, $\text{MnCo}_2\text{O}_4/\text{NF}$, $\text{CuCo}_2\text{O}_4/\text{OMEP}$ and $\text{MnCo}_2\text{O}_4/\text{OMEP}$ electrodes were used as the working electrodes, saturated calomel electrode as the reference electrode and platinum wire electrode as the counter electrode. The electrochemical properties of the composite electrodes were characterized by cyclic voltammetry (CV), charge-discharge analysis (GCD) and electrochemical impedance spectroscopy (EIS).

3. Results

3.1. Material Properties

3.1.1. Electrodes SEM Morphology Analysis

As shown in Figure 1a,b, the Si-MCP composed of millions of neatly arranged porous structures acts as the foundation for making OMEP that compatible with the microelectronics process. After the two-step nickel deposition methods on Si-MCPs, the OMEP (Figure 1c–f) was fabricated with rough morphology and excellent conductivity. SEM images of the $\text{CuCo}_2\text{O}_4/\text{OMEP}$ electrode and the $\text{MnCo}_2\text{O}_4/\text{OMEP}$ electrode are shown in Figures 2 and 3, respectively. The nickel layer deposit on OMEP can make the active material closely adhere to the electrode plate as the nucleation center of CuCo_2O_4 and MnCo_2O_4 nanosheets. Figure 2 shows the images of $\text{CuCo}_2\text{O}_4/\text{OMEP}$ (Figure 2a–d) electrode. The nanoscale CuCo_2O_4 is uniformly deposited on the surface of OMEP, and the micropores of OMEP are retained, which is conducive to the transport of electrolytes inside the electrode. Figure 2e,f shows the sidewall of the $\text{CuCo}_2\text{O}_4/\text{OMEP}$ electrode with different magnification, and the morphologies of the CuCo_2O_4 nanosheets in the cross-section are not the same as the nanosheets on the surface, which may be caused by different solution contact environments in the high aspect ratio channel during the hydrothermal reaction. According to the elemental analysis of the $\text{CuCo}_2\text{O}_4/\text{OMEP}$ electrode from Figure S1a, it is found that the atomic percentage of Ni is 59%. The ratio of Cu, Co and O atoms was close to 1:2:4, which were 6%, 13% and 22%, respectively.

Figure 3 shows the SEM image of $\text{MnCo}_2\text{O}_4/\text{OMEP}$ composite electrode. According to the SEM image in Figure 2a–c, it can be found that MnCo_2O_4 nanosheets are denser than CuCo_2O_4 nanosheets, and these morphological and structural characteristics may cause the loss of specific capacity of MnCo_2O_4 . On the other hand, because MnCo_2O_4 is more compact, there are more active materials per unit area on the $\text{MnCo}_2\text{O}_4/\text{OMEP}$ electrode that achieve a larger surface capacitance than that of $\text{CuCo}_2\text{O}_4/\text{OMEP}$. However, the loose distribution of CuCo_2O_4 nanosheets can reduce the loss of capacitance under high CV scanning speed and large current density. Figure S1b shows the SEM mapping of the $\text{CuCo}_2\text{O}_4/\text{OMEP}$ electrode, from which the atomic percentage of Ni is 39%. Cu, Co and O atoms accounted for 9%, 18% and 34%, respectively. To make a comprehensive analysis of the performance of OMEP as the supercapacitor substrates, the electrodes based on nickel foam were also prepared and characterized under the same conditions. Figures S2 and S3

show the SEM images of CuCo_2O_4 and MnCo_2O_4 deposited on the surface of nickel foam, respectively. From these diagrams, it can be seen that the nanomaterials formed on nickel foam are nanowires, which are completely different from those deposited on the OMEP surface, although their preparation conditions are identical. The above observation and analysis show that the unique substrate structure and surface characteristics can control the morphology of the prepared nanomaterials, and further affect the electrochemical performance of the electrodes.

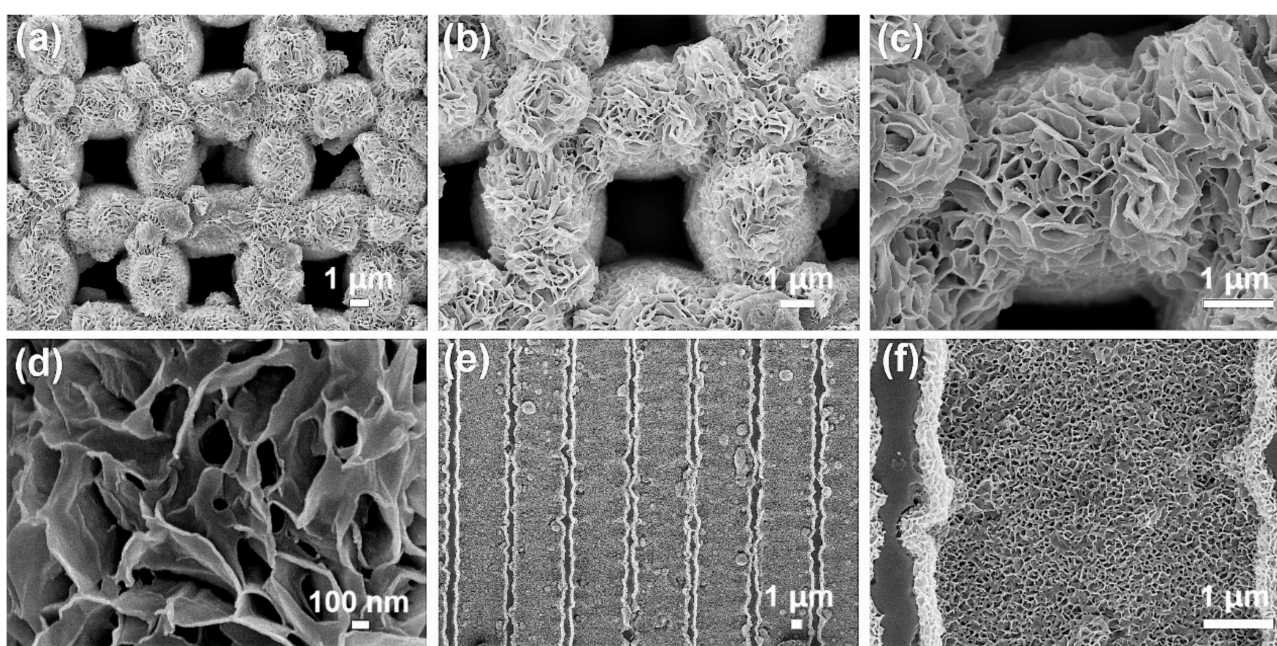


Figure 2. SEM images: (a–d) top surface of CuCo_2O_4 /OMEF with different magnification; (e,f) side wall of CuCo_2O_4 /OMEF with different magnification.

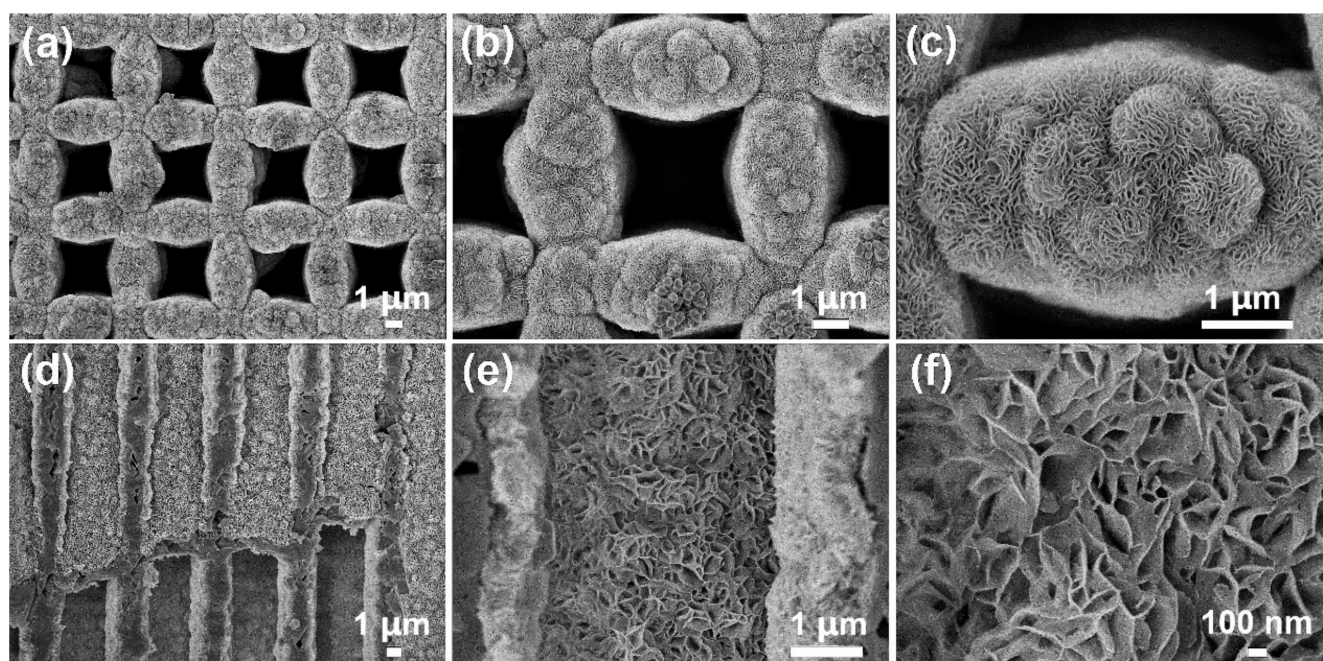


Figure 3. SEM images: (a–d) top surface of MnCo_2O_4 /OMEF with different magnification; (e,f) sidewall of MnCo_2O_4 /OMEF with different magnification.

3.1.2. Electrodes Structure and Composition Analysis

The structures of OMEP and nanocomposite electrodes were determined by X-ray diffraction, as shown in Figure 4a. The XRD pattern of $\text{CuCo}_2\text{O}_4/\text{OMEP}$ and $\text{MnCo}_2\text{O}_4/\text{OMEP}$ has the strong peak of active materials of CuCo_2O_4 and MnCo_2O_4 , respectively. The diffraction peaks of backbone substrate of OMEP only have stronger Ni (JCPDS Card No. 01-089-7128) and Si peaks, indicating that the active materials were successfully deposited on the substrate. By comparing the No. 001-1155 card in JCPDS, it can be verified that the composite electrode is successfully attached with the CuCo_2O_4 material, and the $\text{CuCo}_2\text{O}_4/\text{OMEP}$ composite electrode matches the peaks of the crystal faces (311), (422) and (440) on the No. 78-2177 card in JCPDS of CuCo_2O_4 . The crystal face of CuCo_2O_4 is the highest peak at (311), indicating that the CuCo_2O_4 nanosheets grow preferentially along the direction of (311) [20]. In addition, a dense CuCo_2O_4 nanosheet with a thickness of about 300 nm is covered on the surface of OMEP, which weakens the peak strength of Ni (red line). The pink line is the XRD pattern of the $\text{MnCo}_2\text{O}_4/\text{OMEP}$ electrode. By comparing the No.023-1237 card in JCPDS, the XRD pattern of $\text{MnCo}_2\text{O}_4/\text{OMEP}$ composite electrode matches the peaks of the crystal faces (220), (222), (400) and (422) on the card. The other spikes occur due to the influence of OMEP plates.

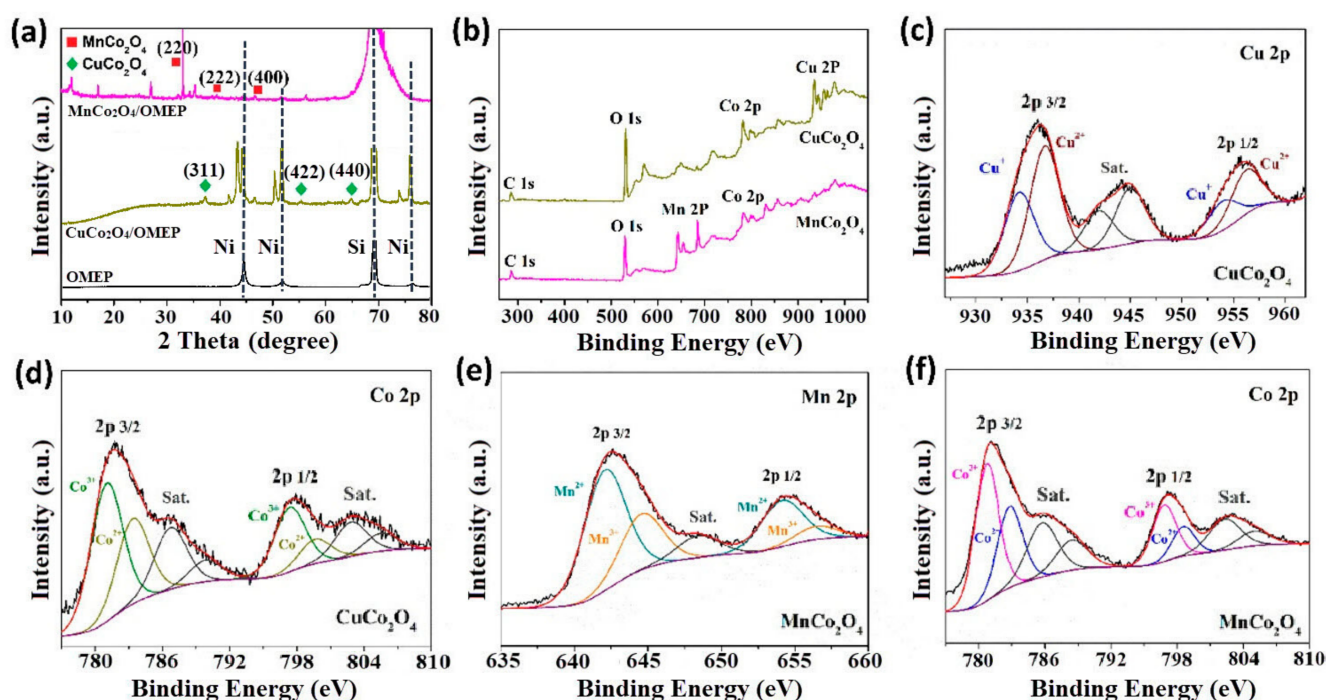


Figure 4. (a) XRD patterns of $\text{CuCo}_2\text{O}_4/\text{OMEP}$, $\text{MnCo}_2\text{O}_4/\text{OMEP}$ and OMEP; (b) XPS survey spectrum of $\text{CuCo}_2\text{O}_4/\text{OMEP}$ and $\text{MnCo}_2\text{O}_4/\text{OMEP}$; XPS spectra of (c) Cu 2p and (d) Co 2p for $\text{CuCo}_2\text{O}_4/\text{OMEP}$; XPS spectra of (e) Mn 2p and (f) Co 2p for $\text{MnCo}_2\text{O}_4/\text{OMEP}$.

Figure S4 and Figure 4b–f provide the XPS general patterns and interval diagrams of the $\text{CuCo}_2\text{O}_4/\text{OMEP}$ electrode and the $\text{MnCo}_2\text{O}_4/\text{OMEP}$ electrode, respectively. By observing Figure 4b, it is found that the peak position of C 1s appears at 285 eV, which is consistent with the XPS standard energy spectrum. In Figure S4, O 1s peaks are subdivided into metal–oxygen bonds (M–O, M: Co, Cu and Mn) and oxygen-containing groups (H–O) [32]. XPS images show that the adsorption of oxygen and hydroxyl groups in CuCo_2O_4 and MnCo_2O_4 crystal on the surface of the nanostructure are the two main factors affecting the nanostructure [33]. Compared the Figure S4a,b, it can be found that the O 1s peak of the $\text{MnCo}_2\text{O}_4/\text{OMEP}$ electrode is shifted to the right, which may be caused by the more abundant valence states of Mn. Figure 4c shows the interval XPS map of Cu 2p. The peak of $\text{Cu } 2p_{3/2}$ appears at 936 eV, and the peak of $\text{Cu } 2p_{1/2}$ at 956 eV. Cu^{2+} and Cu^+ constitute

the main valence states of Cu 2p [19,34]. The corresponding Figure 4e shows the Mn 2p pattern of the MnCo₂O₄/OMEP electrode. The peak of Mn 2p_{3/2} appears at 643 eV, and the peak of Co 2p_{1/2} at 655 eV. Mn²⁺ and Mn³⁺ are the main valence states of Mn 2p [35,36]. Figure 4d,f show that Cu and Mn do not affect the spectral arrangement of Co 2p. The peak of Co 2p_{3/2} appears at 782 eV, the peak of Co 2p_{1/2} at 798 eV and the satellite peaks (Sat.) of Co 2p_{3/2} and Co 2p_{1/2} appear at 787 eV and 803 eV, respectively. Among them, Co³⁺ and Co²⁺ are the main valence states of Co 2p [37].

3.1.3. Electrodes Electrochemical Performance Analysis

The redox reaction principle of CuCo₂O₄ and MnCo₂O₄ nanomaterials in alkaline solution as follows [38,39]:

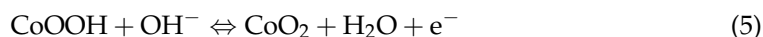
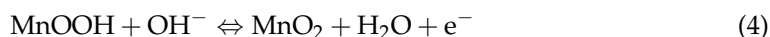
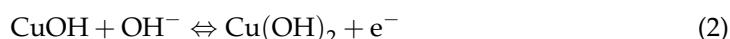


Figure 5 illustrates the CV and GCD results of electrodes based on CuCo₂O₄ and MnCo₂O₄. Figure 5a shows that CuCo₂O₄/OMEP and MnCo₂O₄/OMEP have a much better capacitance than CuCo₂O₄ and MnCo₂O₄ prepared on nickel foam. Correspondingly, the sample based on OMEP has a larger CV disclose area (Figure 5a, 10 mV s^{−1} scan rate) and longer discharge time (Figure 5b, 5 mA cm^{−2} current density). As shown in Figure 5c, the CV curve of the CuCo₂O₄/OMEP electrode presents a rectangle, and the CV curve gradually increases with the increase in scanning speed. Figure 5d depicts the GCD curve of the CuCo₂O₄/OMEP electrode. In the discharge process, the voltage and current of the CuCo₂O₄/OMEP electrode are linear.

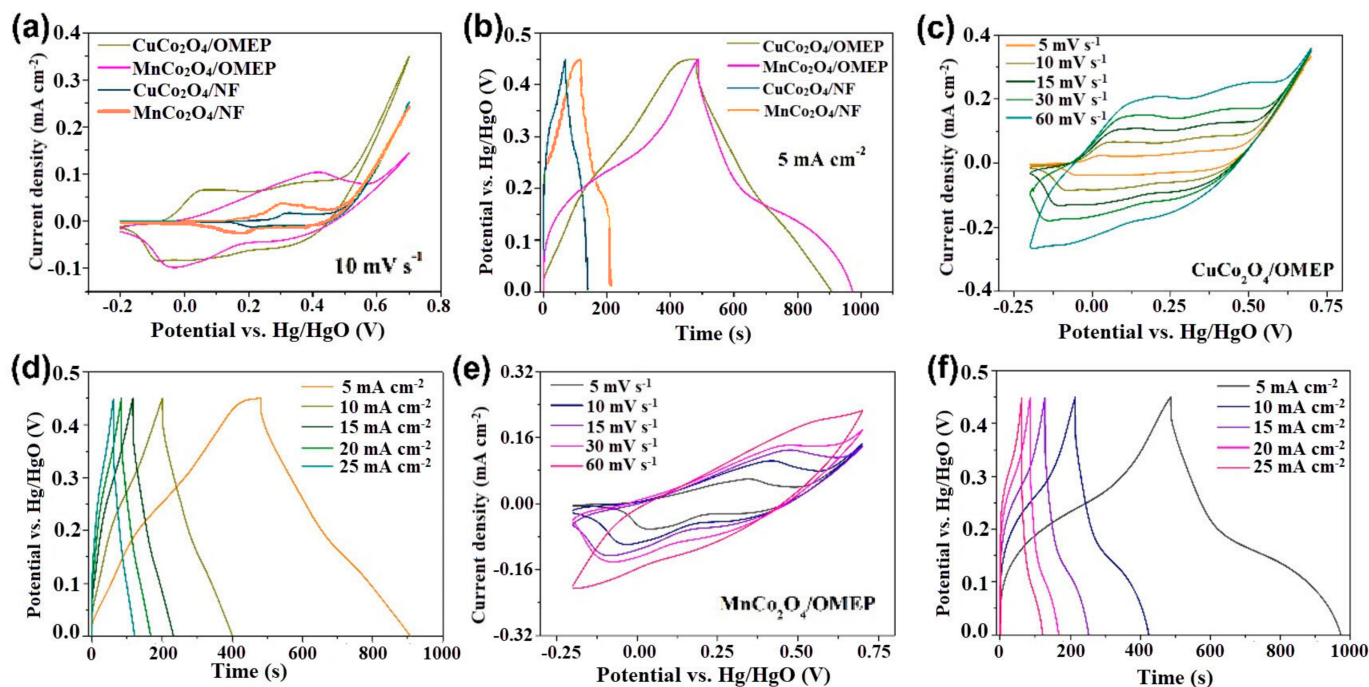


Figure 5. (a) Cyclic voltammetry curves at the scanning rate of 10 mV S^{−1} and (b) 5 mA cm^{−2} charging–discharging curves of the newly fabricated CuCo₂O₄/NF, MnCo₂O₄/NF, CuCo₂O₄/OMEP and MnCo₂O₄/OMEP electrode; CuCo₂O₄/OMEP (c) CV curves at different scanning rates and (d) charging–discharging curves at different current densities; MnCo₂O₄/OMEP (e) CV curves at different scanning rates and (f) charging–discharging curves at different current densities.

In Figure 5e, the redox peak of the $\text{MnCo}_2\text{O}_4/\text{OMEP}$ electrode is obvious. When the scanning speed exceeds 15 mV s^{-1} , obvious deformation occurs in the closed region of the CV curve of the $\text{MnCo}_2\text{O}_4/\text{OMEP}$ electrode. Figure 5f shows the GCD curve of the $\text{MnCo}_2\text{O}_4/\text{OMEP}$ electrode, indicating that the specific capacitance of this electrode is mainly contributed by the double layer capacitance [40]. Figures S5 and S6 reflect electrochemical chemistry performance of $\text{CuCo}_2\text{O}_4/\text{NF}$ and $\text{MnCo}_2\text{O}_4/\text{NF}$ at different CV scanning rates and different current densities after activation. It can be seen from these two pictures that the CV curve and GCD curve of electrodes prepared by the same process on nickel foam are quite different from those based on OMEP. The peaks of the CV curve based on foamed nickel are more obvious, while the OMEP-based electrode curve is more similar to a rectangle, which reflects that OMEP-based samples have more pseudo capacitance components.

To further analyze the positive influence of the fabrication nanomaterials on OMEP and preparation of bimetallic oxides on the performance of supercapacitors, systematic electrochemical tests were also carried out on OMEP and $\text{Co}_3\text{O}_4/\text{OMEP}$. Unlike the CV from $\text{CuCo}_2\text{O}_4/\text{OMEP}$ and $\text{MnCo}_2\text{O}_4/\text{OMEP}$, as shown in Figure 6a, the CV from $\text{Co}_3\text{O}_4/\text{OMEP}$ has a clear redox peak, while $\text{CuCo}_2\text{O}_4/\text{OMEP}$ and $\text{MnCo}_2\text{O}_4/\text{OMEP}$ are more likely to be a surface electrochemical pseudocapacitive reaction at high scanning rates. Figure 6b indicates that $\text{Co}_3\text{O}_4/\text{OMEP}$ has a low specific capacity and surface capacitance because it has fewer active sites and lower conductivity. Figure 6c compares CV curves of OMEP, $\text{Co}_3\text{O}_4/\text{OMEP}$, $\text{CuCo}_2\text{O}_4/\text{OMEP}$ and $\text{MnCo}_2\text{O}_4/\text{OMEP}$ at different scanning speeds. The results show that the CV area of the $\text{CuCo}_2\text{O}_4/\text{OMEP}$ electrode is slightly smaller than that of the $\text{MnCo}_2\text{O}_4/\text{OMEP}$ electrode at low scanning speed (Figure 5a, 5 mV s^{-1}). At the same time, the compact structure of MnCo_2O_4 nanosheets showed a larger surface capacitance. At high scanning speed (Figure 6c, 60 mV s^{-1}), the CV area of the $\text{CuCo}_2\text{O}_4/\text{OMEP}$ electrode is about twice that of the $\text{MnCo}_2\text{O}_4/\text{OMEP}$ electrode. The reverse overrun of the CV area is attributed to the higher conductivity of CuCo_2O_4 nanosheets than that of MnCo_2O_4 nanosheets, and the $\text{CuCo}_2\text{O}_4/\text{OMEP}$ composite structure is more suitable for a high CV scanning speed environment. Figure 6c discloses that the capacitance of $\text{CuCo}_2\text{O}_4/\text{OMEP}$ and $\text{MnCo}_2\text{O}_4/\text{OMEP}$ shows considerably larger capacitance than OMEP and $\text{Co}_3\text{O}_4/\text{OMEP}$ because of the larger enclosed area in the CV curve and longer discharge time (Figure S7, 5 mA cm^{-2} charging–discharging current).

The specific capacitance of the electrode C_s and the surface capacitance of the CV curve C_{CV} can be calculated according to Equations (6) and (7), and the energy (E) and the power (P) density were determined according to the equations as follows [41]:

$$C_s = \frac{I \times \Delta t}{m \times \Delta V} \quad (6)$$

$$C_{CV} = \int idV / (2v \times m \times \Delta V) \quad (7)$$

$$E = \frac{C \times (\Delta V)^2}{2 \times 3.6} \quad (8)$$

$$P = \frac{E \times 3.6}{\Delta t} \quad (9)$$

where $C_s(\text{F/g})$ is the specific capacitance, $I(\text{A})$ is the current density of charge and discharge, $\Delta t(\text{s})$ is the discharge time, $m(\text{g})$ is the mass of the active substance in the electrode and $\Delta V(\text{V})$ is the pressure drop in the test. $v(\text{V/s})$ is the scanning speed of the CV curve. $\int idV$ is the closed area of the CV curve.

According to Figure 5d, Figure 6d and Equation (6), the specific capacitances of the $\text{CuCo}_2\text{O}_4/\text{OMEP}$ electrode are 1199 F g^{-1} (5 mA cm^{-2}), 1111 F g^{-1} (10 mA cm^{-2}), 970 F g^{-1} (15 mA cm^{-2}), 928 F g^{-1} (20 mA cm^{-2}) and 844 F g^{-1} (25 mA cm^{-2}). According to Equation (7), the surface capacitances of the corresponding GCD curve can be further calculated as follows: 4.76 F cm^{-2} (5 mA cm^{-2}), 4.40 F cm^{-2} (10 mA cm^{-2}), 3.85 F cm^{-2}

(15 mA cm⁻²), 3.82 F cm⁻² (20 mA cm⁻²) and 3.49 F cm⁻² (25 mA cm⁻²). It can be found that the surface capacitance of the CuCo₂O₄/OMEP electrode maintains good magnification characteristics, and the surface capacitance is stable at about 2 F cm⁻² at each scanning speed. According to Figure 6d and Equations (6) and (7), the specific capacitances of the MnCo₂O₄/OMEP electrode are 843 F g⁻¹ (5 mA cm⁻²), 728 F g⁻¹ (10 mA cm⁻²), 648 F g⁻¹ (15 mA cm⁻²), 564 F g⁻¹ (20 mA cm⁻²) and 520 F g⁻¹ (25 mA cm⁻²). The surface capacitances corresponding to GCD curves are 5.39 F cm⁻² (5 mA cm⁻²), 4.60 F cm⁻² (10 mA cm⁻²), 4.27 F cm⁻² (15 mA cm⁻²), 3.71 F cm⁻² (20 mA cm⁻²) and 3.25 F cm⁻² (25 mA cm⁻²). The results show that with the increase in scanning rate and current density, the surface capacity of the MnCo₂O₄/OMEP electrode decreases sharply. The specific capacity and surface capacitance of the electrodes mentioned in this paper are shown in Table 1.

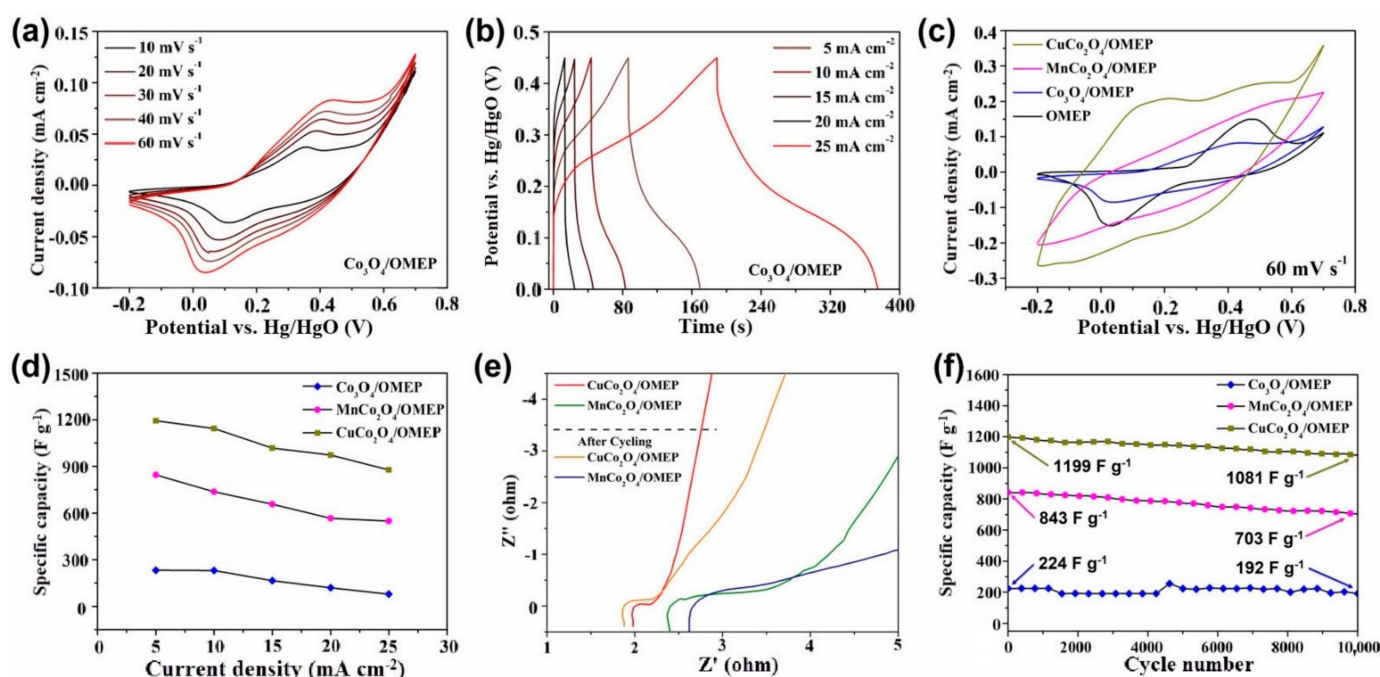


Figure 6. Co₃O₄/OMEP (a) CV curves at different scanning rates and (b) charging–discharging curves at different current densities; (c) Cyclic voltammograms at the scanning rate of 10 mV S⁻¹ of the newly fabricated OMEP, Co₃O₄/OMEP, CuCo₂O₄/OMEP and MnCo₂O₄/OMEP electrode; (d) specific capacity of the electrodes at different current densities (e) Nyquist curve of the composite electrode before and after 10,000 cycle; (f) 10,000 cycle stability test of the series electrode.

Table 1. The specific and area capacity comparison of series electrodes under different current densities.

Current Density (mA cm ⁻²)	CuCo ₂ O ₄ /OMEP (F g ⁻¹ /F cm ⁻²)	MnCo ₂ O ₄ /OMEP (F g ⁻¹ /F cm ⁻²)	CuCo ₂ O ₄ /NF (F g ⁻¹ /F cm ⁻²)	MnCo ₂ O ₄ /NF (F g ⁻¹ /F cm ⁻²)	Co ₃ O ₄ /OMEP (F g ⁻¹ /F cm ⁻²)
5	1199/4.76	843/5.39	322/0.77	249/1.05	263/2.10
10	1111/4.40	728/4.60	259/0.62	225/0.95	226/1.81
15	970/3.85	648/4.27	217/0.52	176/0.74	163/1.30
20	928/3.82	564/3.71	185/0.44	130/0.55	113/0.90
25	844/3.49	520/3.25	150/0.36	110/0.46	74/0.59

It is obvious that due to the compactness of MnCo₂O₄ nanosheets fabricated on OMEP, the mass of MnCo₂O₄ per unit area is larger CuCo₂O₄ on OMEP, so the calculated specific capacity of MnCo₂O₄/OMEP is lower than that of CuCo₂O₄/OMEP. In addition, the area capacitance of the MnCo₂O₄/OMEP electrode is larger than that of the CuCo₂O₄/OMEP electrode at a lower current density (lower than 15 mA cm⁻²). However, the capacitance of the CuCo₂O₄/OMEP electrode exceeds that of the MnCo₂O₄/OMEP electrode in

20 mA cm⁻² and 25 mA cm⁻² charge and discharge tests. The reason for these phenomena is that the arrangement of MnCo₂O₄ nanosheets is too dense, so the MnCo₂O₄/OMEP electrode cannot fully contact the electrolyte at a high charge-discharge speed, resulting in the deformation of the CV curve and the loss of electrical capacity.

Figure 6e shows the EIS pattern of the composite electrode before and after the cycle. It can be observed that the Nyquist curve of the composite electrode consists of an arc in the high-frequency region and an oblique line in the low-frequency region. Among them, the CuCo₂O₄/OMEP electrode (red line) before the cycle has the shortest arc radius and the highest slope of the inclined line in the low-frequency region, which means that the composite electrode has the lowest impedance and the higher conductivity of the CuCo₂O₄/OMEP electrode. In addition, the arc radius (red, green line) in the high-frequency region of the composite electrode before the cycle is smaller than the arc radius (orange, blue line) after the cycle, and the slope of the slope in the low-frequency region is higher than the slope of the slope after the cycle. It shows that after 10,000 cycles, the electrical conductivity of the electrode is lost to varying degrees. It can be seen from the intersection of the Nyquist curve and ordinate zero axis that the solution resistance (R_s) of the CuCo₂O₄/OMEP electrode and the MnCo₂O₄/OMEP electrode before circulation are 2.01 and 2.42 ohms, respectively. After 10,000 cycles, the solution resistance of the CuCo₂O₄/OMEP electrode was reduced to 1.88 ohms, while the solution resistance of the MnCo₂O₄/OMEP electrode was increased to 2.68 ohms.

Figure 6f shows 10,000 cycle stability tests for CuCo₂O₄/OMEP electrodes and MnCo₂O₄/OMEP electrodes. The measured specific capacitances of the CuCo₂O₄/OMEP electrode and the MnCo₂O₄/OMEP electrode at the current density of 5 mA cm⁻² before the cycle is 1199 F g⁻¹ and 843 F g⁻¹, respectively. After 10,000 cycles, the specific capacitance of the CuCo₂O₄/OMEP electrode at the current density of 5 mA cm⁻² is 1081 F g⁻¹, resulting in a 9.8% capacitance loss, while the specific capacitance retention of the MnCo₂O₄/OMEP electrode in the same condition is 83.5%. The above data indicate that the CuCo₂O₄/OMEP electrode is more stable than the MnCo₂O₄/OMEP electrode in terms of cycle stability. This may be due to the introduction of Cu²⁺ and the special structure of CuCo₂O₄/OMEP, which make it difficult to dissolve and agglomerate in the electrolyte.

3.1.4. Electrochemical Performance Analysis of Hybrid Supercapacitor

CuCo₂O₄ and MnCo₂O₄ hybrid supercapacitor devices are prepared by using the MCo₂O₄/OMEP (M=Cu, Mn) as the positive electrode and carbon-based nickel foam as the negative electrode. The electrochemical properties of the two devices are shown in Figure 7. Figure 7a,c shows that the CV curve closing area of MnCo₂O₄/OMEP//AC is larger than that of CuCo₂O₄/OMEP//AC. This is because the active material mass in CuCo₂O₄/OMEP//AC is 2.4 mg, far less than that in MnCo₂O₄/OMEP//AC (4.2 mg). More active material provides higher CV surface capacitance of the supercapacitor. According to Figure 7b and Equations (8) and (9), the power density (energy density) of MnCo₂O₄/OMEP//AC can be calculated as follows: 2.92 KW kg⁻¹ (41.7 Wh kg⁻¹), 5.83 KW kg⁻¹ (30.6 Wh kg⁻¹), 8.75 KW kg⁻¹ (21.1 Wh kg⁻¹), 11.67 KW kg⁻¹ (15.2 Wh kg⁻¹) and 14.58 KW kg⁻¹ (11.7 Wh kg⁻¹). Figure 7d shows the charge-discharge curve of MnCo₂O₄ supercapacitor, and the power density (energy density) can be obtained as follows: 1.67 KW kg⁻¹ (25.9 Wh kg⁻¹), 3.33 KW kg⁻¹ (20.2 Wh kg⁻¹), 5.00 KW kg⁻¹ (16.8 Wh kg⁻¹), 6.67 KW kg⁻¹ (14.6 Wh kg⁻¹) and 8.33 KW kg⁻¹ (11.6 Wh kg⁻¹). The comparison of the power and energy density of the two supercapacitors is shown in Figure 7e. In addition, the cyclic stability test results of the supercapacitor are shown in the lower-left corner of Figure 7e. The test showed that after 10,000 cycles, the CuCo₂O₄ supercapacitor maintained a specific capacitance of 92.5%, while the MnCo₂O₄ supercapacitor maintained 90.2% capacitance.

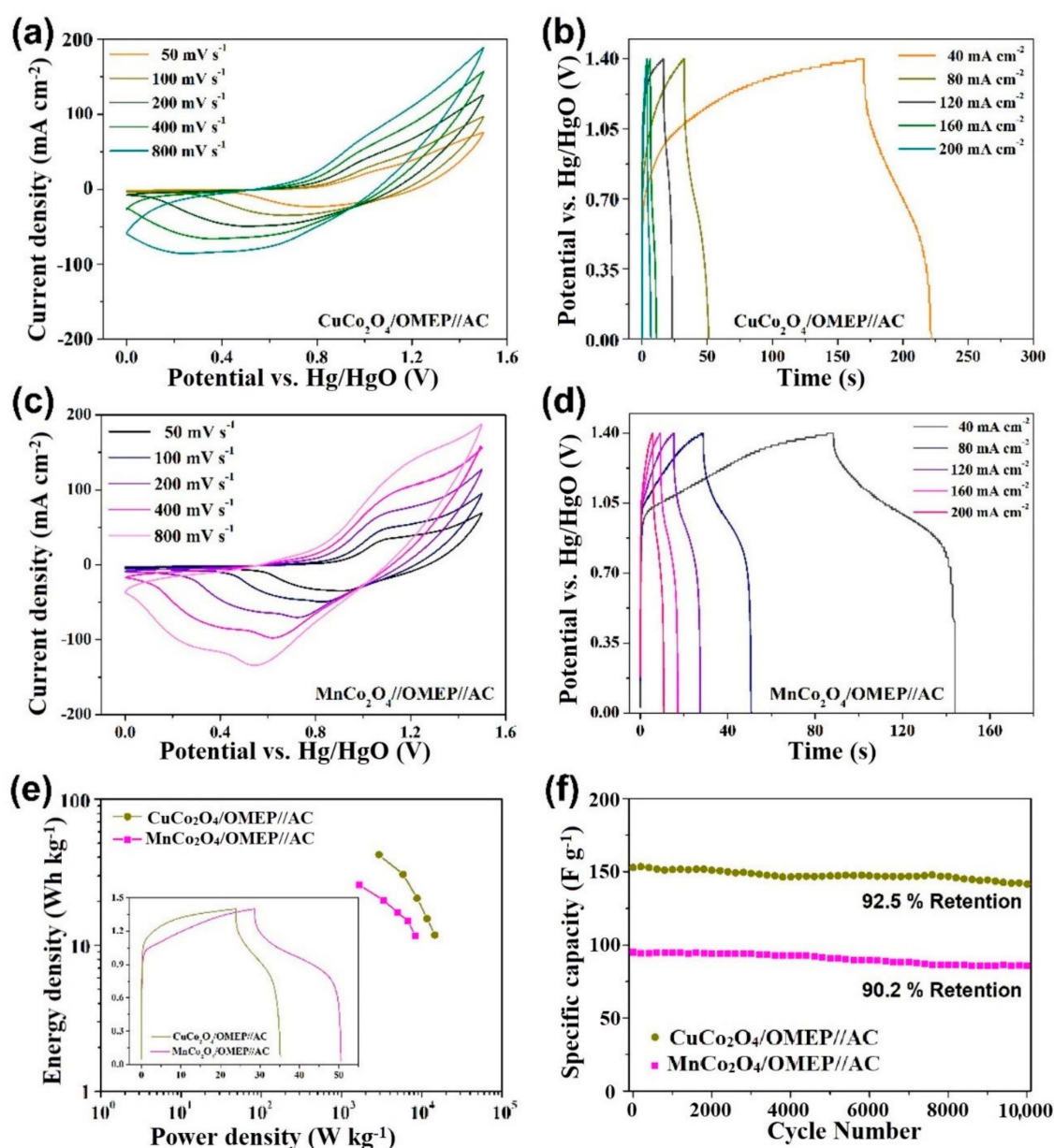


Figure 7. Electrochemical performance test of (a) CV curves and (c) GCD curves of CuCo₂O₄/OMEP//AC; (b) CV curves and (d) GCD curves of MnCo₂O₄/OMEP//AC; (e) Ragone plot of the as-assembled ASC (insets is the comparison of GCD curves from the as assembled ASC before and after 10,000 cycles); (f) cycling stability of the 10,000 cycles of devices at large current densities.

4. Conclusions

AB₂O₄-type binary-transition metal oxides (BTMOs) of CuCo₂O₄ and MnCo₂O₄ were successfully prepared on ordered macroporous electrode plates (OMEP) that are compatible with silicon micro-nano processes for supercapacitors. These composite porous electrodes have a unique three-dimensional structure, which facilitates the transport of electrons and ions increases the liquid–solid interface area, improves the active material utilization efficiency and reduces the weight and size of the electrode, which allows the active material to obtain a large specific capacitance. The CuCo₂O₄/OMEP has a capacitance of 1199 F g⁻¹ at the current density of 5 mA cm⁻² and 844 F g⁻¹ at the current density of 5 mA cm⁻². After 10,000 cycles, the capacitance stability achieved 92.5%. The asymmetric supercapacitor device of CuCo₂O₄/OMEP//AC achieves a power density of 14.58 kW kg⁻¹ at the energy density of 11.7 Wh kg⁻¹. The MnCo₂O₄/OMEP electrode

shows a better area capacitance at a small current density (5.76 F cm^{-2} at 5 mA cm^{-2}) because its compact structure can load more active substances per unit area. The MnCo_2O_4 supercapacitor's power density is 8.33 kW kg^{-1} with an energy density of 11.6 Wh kg^{-1} and its cycle stability was 90.2%, maintained after 10,000 cycles.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/su13179896/s1>, Figure S1: SEM mappings of (a) the CuCo_2O_4 /OMEP electrode; (b) the MnCo_2O_4 /OMEP electrode, Figure S2: SEM images: (a–d) CuCo_2O_4 nanostructures fabricated on nickel foam with different magnification, Figure S3: SEM images: (a–d) MnCo_2O_4 nanostructures fabricated on nickel foam with different magnification, Figure S4: XRD patterns of O s1 for (a) CuCo_2O_4 /OMEP and (b) MnCo_2O_4 /OMEP, Figure S5: (a) CV curves of CuCo_2O_4 /NF at different scanning rates and (b) charging–discharging curves of CuCo_2O_4 /NF at different current densities after activation, Figure S6: (a) CV curves of MnCo_2O_4 /NF at different scanning rates and (b) charging–discharging curves of MnCo_2O_4 /NF at different current densities after activation, Figure S7: charge–discharge curves of the newly fabricated OMEP, Co_3O_4 /NF, CuCo_2O_4 /OMEP and MnCo_2O_4 /OMEP electrode at a current density of 5 mA cm^{-2} .

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