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A robust NiCo₂O₄/superactivated carbon aqueous supercapacitor with high power density and stable cyclability

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Abstract

Herein we investigate the performance of an aqueous asymmetric supercapacitor (AAS) assembled using a novel nanostructured NiCo₂O₄ as positive electrode and a polymer derived superactivated carbon (SAC) as negative electrode. The combination of both the nanostructured NiCo₂O₄ and the carbon with hierarchical porosity and ultrahigh specific surface area (above 3000 m² g⁻¹) lead to excellent rate performances and long stability of the system. The optimization of the AAS device is further achieved through the variation of mass ratio between positive and negative electrodes. Optimized AAS full cell exhibits reversibility within the 0.0-1.5 V operative voltage region delivering a specific cell capacity of 24.6 mAh g⁻¹ at current density of 1 A g⁻¹. This results in a remarkable energy density of 13 Wh kg⁻¹ at a power density of 26.2 kW kg⁻¹ and an excellent cycling durability above 87% of the initial capacity after 10,000 charge-discharge cycles.

Introduction

Electrochemical energy storage devices, such as batteries and supercapacitors, have drawn significant attention in the recent years due to their extensive use in portable electronics, random access memory back-up devices, industrial power/energy resources, hybrid electric vehicles and so forth.^[1-3] In particular, electrochemical capacitors, also known as supercapacitors, exhibit higher power density than Li-ion batteries (LIBs) (10^3 - 10^4 W kg⁻¹ vs. 80-250 W kg⁻¹, respectively) and higher energy density than conventional capacitors (5 Wh kg⁻¹ vs. 0.2 Wh kg⁻¹, respectively).^[1-5] These features are complemented with their excellent cycle life ($> 10^6$ cycles), rapid charge/discharge (within few seconds), low maintenance cost and safety. Supercapacitors can store energy by two different mechanisms: (i) the non-Faradic electrostatic adsorption of electrolyte ions by the formation of an electric double layer, or (ii) through fast and highly reversible Faradic redox reactions on the electrode surface (pseudocapacitance). These two mechanisms can be configured and utilized either symmetrically or asymmetrically in an electrochemical capacitor device.^[6]

Supercapacitors based on aqueous electrolytes with high ionic conductivity, are non-flammable, cheaper and are more environmental friendly than those ones operating with organic electrolytes.^[7] In contrast, aqueous symmetric supercapacitors (ASS) show lower energy density compared to organic- or ionic liquid-based systems due to their narrower electrochemical stability window. Therefore, it is a tremendous challenge to improve the energy density of aqueous electrochemical capacitors without compromising its environmental benignity, cost and power density. On this note, aqueous asymmetric supercapacitor (AAS) combining a battery-type positive electrode and an EDLC-type

negative electrode has allured widespread attention in the energy storage field, becoming an inexpensive alternative or supplement to LIBs in many applications.^[7]

For the positive electrode, various pseudocapacitive materials including mono or multi-metallic transition compounds and conductive polymers have been thoroughly investigated due to their excellent charge storage capability by reversible redox reactions.^[4,7,8] Some transition monometallic oxides (RuO_2 , MnO_2 , V_2O_5 , NiO , Co_3O_4 or Fe_3O_4) have been considered as positive electrode materials for AAS systems. The major drawback of most of these materials (with the exception of RuO_2) is their low electronic conductivity, which leads to fast surface degradation at high current rate and repeated charge-discharge operations.^[1,3] The use of multi-metallic compounds such as Mn-Co, Co-Ru, Co-Mo, Co-Al, Ni-Zn-Co and Ni-Co has been found to alleviate this drawback,^[9-14] and specific capacities about 2-5 times higher than those provided by monometallic oxides have been reported.^[7,15] Among them, a binary metal oxide, $\text{Ni}_x\text{Co}_{(3-x)}\text{O}_4$, has been discovered to hold tremendous promise due to its excellent theoretical capacity (over 2000 F g^{-1} in terms of capacitance) along with high electronic conductivity, facilitating a higher rate performance compared to its monometallic counterparts.^[16-18] Moreover, nano-sized positive electrode materials are highly desired, since redox active functional groups concentration is maximized and its accessibility is improved, leading to better rate performances and reversibility.^[19-25]

Regarding the negative electrode activated carbons are traditionally chosen as negative electrodes for AAS because of their high specific surface area, chemical stability, good conductivity and low cost.^[26-27] However, the large concentration of ultramicropores (pore size $<0.7 \text{ nm}$) and tortuous microporosity, inherent to the activation processes of

preformatted rigid precursors using steam, CO₂, KOH or NaOH,^[28] strongly decrease their performance at high current rates, resulting in a failing balance of the high capacity exhibited by the positive electrodes;^[7,8] so, alternative nanostructured carbons such as stacked graphene films, graphene oxides or carbon nanotubes have been also postulated as promising candidates for the negative electrode.^[4-5] In this context, in our previous work, we introduced a novel and straightforward synthetic process to easily obtain a very high surface area carbon by the simultaneous polymerization, carbonization and chemical activation of a mixture of melamine and terephthalaldehyde with KOH. These super-activated carbons showed an excellent performance when tested as active electrode material in symmetric EDLCs using different aqueous electrolytes.^[29] The combination of high specific surface area and its hierarchical pore structure at the meso- and micropore scale favors the ion transport making of it an excellent candidate to be used as negative electrode material for high power asymmetric energy storage devices.

Additionally, to the performances of the individual electrode materials, the mass balance between positive and negative electrodes also plays a key role on the electrochemical performance of the resultant advanced hybrid full cells. The mass balance allows controlling the potential span and degree of utilization of each electrode within the asymmetric cell, and is the key to achieve a high energy density with high cycle life without compromising the power density. Within this context, in this work, we have investigated the performance of a robust AAS cell assembled using a homemade ultrahigh specific surface area carbon as the negative electrode and a nanostructured NiCo₂O₄ as the positive electrode (a combination of EDLC and faradaic type materials), and the impact of the electrode mass balance on the electrochemical performance of the system.

Results and Discussion

The structure and morphology of the NiCo_2O_4 was studied by scanning electron microscopy (SEM). Figure 1A clearly shows that the material is composed of dendritic microspheres formed by the assembly of NiCo_2O_4 nanothorns. Figure S1A from the Supporting Information clearly shows that the hollow core morphology of these floral spheres wall is a tightly packed bundle of nanothorn-like crystalline sheets of NiCo_2O_4 . These types of self-assembled hierarchical structures are generally obtained by hydro/solvothermal synthesis where urea plays the role of both the self-template organizer and the precipitator. Meanwhile, in figure 1B, transmission electron microscopy (TEM) images reveal that the thorn bundles are decorated with a stone-pillar-like array with well-defined porous structures, which may help the electrolyte ions accessing the surface. The inset of figure 1B indicates the well-distinct polycrystallinity of each grain with the spacing between the adjacent fringes of ~ 0.273 nm, which is in agreement to the theoretical (111) interplane distance within the NiCo_2O_4 spinel phase. Furthermore, figures S1B and S1D show the prominent morphology of these nanothorn bundles.

Figure 1. (A) SEM image (inset: higher magnification SEM image of the sphere surface), (B) TEM image (inset: high magnification TEM image) (C) XRD pattern and (D) Nitrogen adsorption desorption isotherms (inset: pore size distribution curve) of NiCo_2O_4 .

The X-ray diffraction (XRD) pattern registered for the synthesized nickel cobalt oxide is depicted in Figure 1C. As it can be observed, the pattern shows well-defined diffraction peaks at 18.9° , 30.9° , 36.6° , 44.6° , 55.4° , 59.0° and 64.8° , which can be assigned to the (111), (200), (311), (400), (422), (511) and (440) lattice planes indexed for the crystalline NiCo_2O_4 according to the standard JCPDS file no. 73-1702. It is worth noting that only these peaks are observed, discarding the presence of other crystalline impurity phases in the sample. According to Energy dispersive X-ray (EDX) analysis (Figure S1C), the

atomic ratio between Ni and Co is similar to the ratio used in the pristine solution media and in good agreement with the formation of crystalline NiCo_2O_4 spinel. To get more information on the textural properties of this sample, the oxide was investigated by nitrogen gas adsorption–desorption technique. The isotherm registered for the NiCo_2O_4 , shown in figure 1D, exhibits a profile in between type II and type IV according to the IUPAC classification,^[30] with a small hysteresis loop (H3) in the relative pressure region between 0.4 and 1.0. These isotherms are characteristic of mesoporous materials containing slit-shaped pores. It is worth to highlight the quite large BET specific surface area calculated for this mixed metal oxide that reached $255 \text{ m}^2 \text{ g}^{-1}$. The pore size distribution calculated from the adsorption branch through the Barrett–Joyner–Halenda (BJH) approach shows a bimodal distribution with two pore systems centered at $\sim 4.0 \text{ nm}$ and $\sim 22 \text{ nm}$, which correspond to the interparticle voids between primary crystalline particles within the thorns and to the pores between adjacent thorns in the NiCo_2O_4 flowers, respectively, giving rise to a total pore volume of $0.56 \text{ cm}^3 \text{ g}^{-1}$.

The nitrogen adsorption-desorption isotherm registered for the SAC is shown in figure 2A. This isotherm shows a profile between type I and II with a H4-type hysteresis loop according to the IUPAC classification.^[30] The adsorption at high relative pressures indicates the presence of medium size or large mesopores in SAC. The BET specific surface area and pore volume of SAC are calculated to be $3071 \text{ m}^2 \text{ g}^{-1}$ and $2.8 \text{ cm}^3 \text{ g}^{-1}$, respectively. The inset of figure 2A depicts the pore size distribution curve of this carbon, which clearly shows that SAC comprises a bimodal distribution of micro-mesopores with pores of 1-3 nm combined with mesopores ranging from 4.5 to 8 nm.

Figure 2 (A) Nitrogen adsorption desorption isotherms (inset: pore size distribution curve), (B) SEM image and (C) TEM image registered for the SAC, (D) XRD pattern (inset: Raman spectrum).

A more detailed structural characterization of this carbon was performed by SEM and TEM analysis. The SEM image (figure 2B) illustrates the rough surface of the carbon showing irregular-shaped carbon particles of approximately ~ 50 nm. The inter-particle voids in carbon can be the reason for the high content of mesopores in this material ($1.8 \text{ cm}^3 \text{g}^{-1}$), which overall endows the SAC with a good amount of hierarchical porosity at different pore lengths. On the other hand, the high-magnification TEM image (figure 2C) shows the presence of maggot-like shaped nanopores randomly distributed along the

sample. The XRD pattern of the SAC in figure 2D shows a smooth profile without the presence of any significant diffraction peak, which is characteristic of the highly porous amorphous carbons. The Raman spectrum registered for the SAC (inset of figure 2D) shows a typical profile of amorphous carbons; two predominant bands at nearly 1350 cm^{-1} and 1580 cm^{-1} , which correspond to the D and G bands respectively, are observed together with a broad and low intense peak recorded at 2700 cm^{-1} which is ascribed to the G stretching mode. The D band is generally activated by surface defects and it is used to measure the degree of disorder within the carbon materials whereas G band results from the bond stretching vibration of sp^2 carbon pairs.^[29, 31] Furthermore, the presence of the G band in carbon-based materials indicates the perfection of hexagonal symmetry which leads to the formation of a partially graphitic structure. The obtained spectrum supports the amorphous nature characteristic of carbon walls, which contains a large number of defects and pores, which is in good agreement with the XRD measurement.

Electrochemical characterization

The electrochemical activity of the synthesized nanostructured NiCo_2O_4 was firstly investigated in a three-electrode configuration using a 6M KOH aqueous solution as the electrolyte. Figure 3A displays the CV curve registered for the working electrode containing NiCo_2O_4 at a sweep rate of 5 mV s^{-1} in the potential range between 0V and 0.6 V vs. Hg/HgO. A pair of well-defined cathodic and anodic peaks are observed at ca. 0.38 V and 0.27 V.^[32] Another pair of small yet distinguishable redox peaks can also be observed around 0.44 V and 0.36 V vs. Hg/HgO.

All these peaks can be ascribed to the reversible redox transitions between $\text{Co}^{3+}/\text{Co}^{4+}$ and $\text{Ni}^{2+}/\text{Ni}^{3+}$, which under alkaline conditions undergone according to reaction 1 and 2.^[32-34]

With the increase of the scan rate, the oxidation peaks of the CV curve shift towards more positive potentials while the reduction peaks shift to the negative direction (Figure 3B), indicating some uncompensated resistance in the cell, most likely due to the slow redox kinetics, as previously reported elsewhere.^[33] Figure 3C displays the galvanostatic discharge curves of the NiCo_2O_4 floral spheres at different current densities from 1 to 20 A g^{-1} in the 0.0–0.50 V potential range. The non-linear characteristic of the discharge curves proves that this material has battery-like faradaic charge storage behavior rather than pseudocapacitive. Nevertheless, the cell exhibited a specific capacity of 37 mAh g^{-1} at a discharge rate of 1 A g^{-1} and an excellent capacity retention of ~66% at the high current density of 20 A g^{-1} . These results suggest that the porous architecture of this binary metal oxide electrode is ideally suited as a positive electrode material for fast and efficient AAS.

Figure 3. (A) CV curve registered at 5 mV s⁻¹ and (B) at higher sweep rates (10-100 mV s⁻¹) for the NiCo₂O₄. (C) Galvanostatic discharge curves recorded at indicated current densities (1-20 A g⁻¹) and (D) Capacity evolution vs. Current for the NiCo₂O₄.

The electrochemical performance of SAC electrodes was tested in the two-electrode configuration using 6M KOH aqueous solution as electrolyte. Figure 4A shows the CV profiles at various scan rates ranging from 5 to 100 mV s⁻¹ between 0 and 1.0 V. All of the CV curves show large areas with near rectangular-like shapes, which is a characteristic feature for an ideal EDLC behaviour with good dynamic charge propagation.^[29] A sharp change in capacitive current transient upon altering the polarization direction near voltage limits (0.0 and 1.0 V) signifies a very low internal resistance of the cell. This can be

attributed to the presence of a high amount of medium or large-sized mesopores and the high electrical conductivity of the SAC-based electrode. The SAC comprises a bimodal micro-meso porosity which promotes an unrestricted access of electrolyte ions to the available active surface. This highly porous carbon framework helps adsorbing more electrolyte ions on the active electrode surface and also ensures the efficacy of double layer capacitance.^[31]

Figure 4. (A) CV curves registered at 5 mV s⁻¹ (black), 30 mV s⁻¹ (red), 50 mV s⁻¹ (blue) and 100 mV s⁻¹ (pink), (B) charge-discharge curve at labeled current densities, inset shows a magnified view of the 0.8-1.0V region, and (D) specific capacitance evolution of SAC sample at different current rates.

Galvanostatic charge-discharge (CD) curves were registered for SAC at various current densities between the 0.0 and 1.0 V voltage range and plotted in figure 4B. It is worth noticing that this material exhibits a triangular CD profile with almost 100% of coulombic efficiency (*i.e.* charge time = discharge time) and a very low ohmic drop even at very high current rates (see the inset in figure 4B). The specific capacitance value calculated for this sample at 1 A g⁻¹ corresponds to 250 F g⁻¹, and it shows an excellent capacitance retention up to 220 F g⁻¹ at a high current density of 30 A g⁻¹. The excellent rate capability exhibited by this carbon, as evidenced by the high capacitance retention of ~88% of its initial value at 30 A g⁻¹ (Figure 4C) supports the consideration of the SAC carbon as an attractive candidate to be used as negative electrode for AAS system.

Electrochemical performance of the NiCo₂O₄//SAC asymmetric supercapacitor

AAS full cells were fabricated by assembling nanostructured NiCo₂O₄ and SAC as positive and negative electrodes, respectively, and using a 6M KOH aqueous solution as the electrolyte. To evaluate and optimize the electrochemical performance of the AAS cells, four different mass ratios *i.e.*, 1:1, 1:2, 1:3 and 1:4 of positive vs. negative electrodes respectively were investigated by changing only the negative electrode mass with respect to a fixed positive electrode mass. It was observed that increasing the mass of the negative electrode has a noticeable impact on the overall performance of the asymmetric cells. Fig.5A and 5B show CV curves registered for the AAS cells assembled using different electrode mass ratios at low and high scan rates of 5 and 100 mV s⁻¹ in the 0.0-1.5 V potential range. All of the AAS cells exhibit a combinative CV geometry consisting of both faradaic and EDLC type contribution. Some prominent redox peaks can be

observed in the voltage range of 0.8 to 1.5 V resulting from faradaic charge storage in the positive electrode, whereas the potential below 0.8 is mostly non-faradaic in nature. CV curves registered for the individual electrodes in their respective operating potential range within the asymmetric full cell are depicted in figure S2 of the supplementary information. No oxygen evolution was observed at a voltage of 1.5 V, which is estimated to be the appropriate operating potential for an AAS device. As can be observed, the charging and discharging current densities gradually increase as the sweep rate is increased indicating the fast-kinetic reversibility of this AAS system. [35]

Figure 5. (A) Comparative CV profiles at low potential scan rate of 5 mV s⁻¹ and (B) high scan rate of 100 mV s⁻¹, (C) Comparative discharge curve at current density of 1 A g⁻¹ and (D) rate capability of AAS device [NiCo₂O₄//SAC].

The specific capacity and rate capability of these AAS cells was determined by means of galvanostatic charge-discharge tests at different current rates within the 0.0-1.5 V voltage range. Figure 5C shows the comparative discharge profiles corresponding to the AAS cells with different mass ratios registered at 1 A g⁻¹. As can be clearly observed, all of them exhibit a non-linear potential vs. time profile, which indicates the contribution of faradaic battery-type storage mechanisms. Figure 5D shows the variation of the calculated specific cell capacities of the AAS cells for different current densities up to 30 A g⁻¹. It is found that the capacity retention at high current rates of all the AAS cells, except for the 1:1 ratio, is very high, which could be ascribed to the praiseworthy contribution from SAC by generating fast electron conduction path as well as a good stability. Another figure showing the evolution of the specific capacitance in farads per gram is included in the figure S3 of the supplementary information for the sake of comparison with other works reporting charge stored of AAS as specific capacitance. It is also found that there is a significant enhancement of electrochemical capacity up to 1:2 (positive:negative) mass ratio, reaching specific capacity values of 24.6 mAh g⁻¹ at 1 A g⁻¹ and 15 mAh g⁻¹ at 30 A g⁻¹ (figure 5D). No further improvement is observed by increasing the mass of the negative electrode, which is in agreement with the theoretical calculations based on the principle of charge balance ($Q_+ = Q_-$) for each electrode. In this AAS cell, the mass of the negative electrode is large enough to balance the capacity of the positive electrode. Further increase in the mass of the negative electrode (up to four times higher than that of the positive electrode), becomes ineffective to increase the cell capacity. The electrochemical behaviour of 1:3 and 1:4 ratio AAS cells is not hugely different from that of the optimized 1:2 ratio, but when it comes to 1:1 ratio, the capacity performance is

much lower (see table 1). This clearly indicates that, in this case, there is not enough available mass of the negative electrode to fully balance the capacity of the positive electrode, which evidences the importance of the mass balance approach in a full cell asymmetric device. This difference in performance is also manifested from the equivalent series resistance (ESR) vs. current density plots of the AAS cells, in which the 1:1 ratio shows a much higher ESR compared to the negligible values of the other cells (Figure S4 in the supplementary file). Figure 6A demonstrates the cycling performance of 1:2 ratio AAS cell at 5 A g^{-1} current density, where it can be observed that the specific cell capacity increases steadily during the initial 200 cycles. This slight activation process could be ascribed to the gradual penetration of the electrolyte into the active material surface.^[36-37] Subsequently, after reaching the maximum capacity at around 200 cycles, it decreases slowly. After 10000 cycles of charge-discharge, this AAS cell still delivered 87% of its initial capacity, which is an outstanding cycling performance compared to the reported results in similar AAS systems.^[33,35] Such high stability can be attributed to its unique material morphology, which can resist the volume changes in the positive electrode upon electrolyte insertion/deinsertion.^[32-37] Additional stability tests were performed under floating potential (figure S5). This procedure can be considered a more realistic evaluation for cells and further confirms the outstanding stability of this optimized AAS even under this harsh cycling conditions. Figure 6B represents the Ragone plots of the corresponding energy vs power densities for all of the AAS cells. The cell with the 1:2 ratio achieved a high energy density of 24.3 Wh kg^{-1} at a power density of 1.0 kW kg^{-1} (current density of 1 A g^{-1}). Furthermore, this cell still retains 13 Wh kg^{-1} energy density value at high power density of 26.2 kW kg^{-1} , which is very promising. Table S1 of the supplementary file

summarizes the electrochemical performance of this 1:2 ratio AAS cell, compared with other recently reported results in similar AAS devices.

Figure 6. (A) Cycling stability of 1:2 AAS device [NiCo₂O₄//SAC] measured at 5 A g⁻¹ and (B) comparative Ragone plots calculated for the AAS device [NiCo₂O₄//SAC] assembled using labeled mass balances.

Table 1. Comparative electrochemical parameters calculated for the different AAS devices.

AAS device electrode name (Positive//Negative) [NiCo ₂ O ₄ //SAC]	Capacity, Q _D (mAh g ⁻¹)	Coulombic efficiency (η)	ED (Wh kg ⁻¹) ^[a] & PD (kW kg ⁻¹) ^[b] at Current Densities			
				1 A g ⁻¹	10 A g ⁻¹	20 A g ⁻¹
1:1	12.9	71.5	ED	12.0	7.5	3.6
			PD	0.8	5.0	7.4
1:2	24.6	88.1	ED	24.3	20.7	18.4
			PD	1.0	5.1	10.0
1:3	17.3	87.1	ED	17.3	13.7	11.2
			PD	1.0	5.5	10.1
1:4	13.9	85.3	ED	13.8	10.1	8.05
			PD	1.0	5.2	9.85

[a] ED: Energy density. [b] PD: Power density

It can be observed that the present [NiCo₂O₄//SAC (1:2)] device outperforms most of the previously reported AAS cells not only in terms of energy and power densities, but also in terms of much better cycling stability. We have also compared our best AAS results with commercially available Norit carbon by maintaining same mass balance and found

that SAC carbon shows better performance than Norit carbon, which predicts our lab synthesized SAC carbon has much more potential to provide long-term stability (see Figure S6 and table S1 of Supplementary Information). This result confirms that, through a judicious selection of the positive and negative electrodes and a careful balance between the electrode masses, we can successfully design advanced competitive, low-cost aqueous hybrid supercapacitor system.

Conclusions

The present work shows the energy storage potential of a novel aqueous asymmetric system, which is formed by coupling a superactivated carbon as the negative electrode and a nanostructured NiCo_2O_4 as the positive electrode. It also highlights the impact of the mass balance between both electrodes for the optimum performance of the system. The electrochemical studies evidence the importance of the hierarchical structures of the active materials to maintain a good capacity retention at high current densities. The optimization of the electrodes mass balance within the AAS devices leads not only to both excellent energy and power densities but also to outstanding cycling stability. It was found that the best positive: negative mass ratio in this particular AAS device is 1:2, which allows delivering a maximum gravimetric energy density of 24.3 Wh kg^{-1} at 1.0 kW kg^{-1} and 13 Wh kg^{-1} at 26.2 kW kg^{-1} . Additionally, this AAS device exhibits an excellent long-term cycling stability over 10,000 cycles with only a 13% capacity decay, which is outstanding among its peers.

Experimental Section

Synthesis

The super-activated carbon (hereafter denoted as SAC) was synthesized as previously described elsewhere.^[29] Briefly, 1.24 g of melamine, 1.36 g of terephthalaldehyde and 5.0 g of KOH were finely ground in an agate mortar and then directly heated in the furnace at 250°C for 3 h and then at 800°C for 1 h with a heating ramp of 1°C min⁻¹ in Ar atmosphere. The carbonized material was washed several times with 3M HCl and DI water, then dried at 120°C in an oven.

NiCo₂O₄ was synthesized in the following way: 0.126 g of Ni(NO₃)₂·6H₂O, 0.251 g of Co(NO₃)₂·6H₂O and 0.462 g of urea were mixed under continuous stirring for 30 min in 10 ml of DI water. Then, the clear solution was poured in a teflon-lined autoclave and kept in oven for 180°C for 2 h. The purple precipitates were collected by centrifugation and washed with ethanol and DI water several times. After drying at 60°C for 6 h, the samples were calcined in air at 300°C for 3 h.

Physicochemical Characterization

X-ray diffraction (XRD) patterns were recorded on Bruker D8 X-ray diffractometer for powdered samples and the data were attained at 40 kV and 30 mA using CuK α radiation over 2 θ within the range from 5 to 90° at steps of 0.02° with residence time of 5 seconds. Raman spectra data were recorded by a Renishaw spectrometer (Nanonics Multiview 2000), operating with an excitation wave-length of 532 nm under an Ar ion laser. The spectra were assimilated with an exposition time of 10 seconds of the laser beam to the sample. The morphology of the synthesized samples was recorded on Scanning electron

microscope (SEM) in a field emission Quanta 200 FEG microscope. For microstructural characterization, Tecnai G2 transmission electron microscope (TEM, FEI) was operated. For TEM characterization, the powder samples were dispersed in ethanol for 10 min by ultrasonication. Then a few drops of the solution were casted on a holey carbon films framed by a Cu grid. N₂ adsorption-desorption isotherms were measured at -196°C using ASAP 2020 instrument from Micromeritics. Samples were outgassed at 250 °C for 3 h before the analysis. Specific surface area values of all the samples were calculated using BET equation within a range of relative pressure 0.05-0.2, where $p/p_o = 0.95$ was used to calculate the total pore volume (V_T). The micropore volume (V_{mic}) was obtained by applying the Dubinin-Radushkevich equation. The mesopore volume (V_{mes}) was found from the difference between micropore volume and total pore volume. Pore size distribution (PSD) were estimated using from the data of N₂ adsorption branch assuming a slit-shaped pore model and Barrett–Joyner–Halend (BJH) method.

Electrochemical characterization

Electrochemical performance of NiCo₂O₄ was first assessed in a conventional three-electrode configuration using a 6M KOH aqueous solution as electrolyte. The electrodes were prepared by mixing 60 wt% of NiCo₂O₄ with 30 wt% of carbon black (CB) and 10 wt% of polytetrafluorethylene (PTFE) in the presence of a few drops of ethanol. The dough was kneaded continuously until reaching plasticity, uniformly rolled until a thickness of nearly 40 µm, punched out into disk shaped (12 mm in diameter) and finally dried at 120°C overnight. Working electrodes were prepared by compressing these disk-shaped electrodes (~2.12 mg cm⁻²) onto a 2 mm thick Nickel foam (99.8% pure, MTI

Corp.) that served as current collector. A Pt coiled wire and a Hg/HgO (saturated in 1M NaOH) electrode were used as counter and reference electrodes, respectively. The counter electrode was cleaned prior the measurements with acidic piranha solution to remove any surface impurities.

Symmetric SAC//SAC supercapacitors were built using a two-electrode configuration and electrodes with similar masses ($\sim 2.3 \text{ mg cm}^{-2}$) were assembled into Swagelok™-type cells. The disk-shaped electrodes with $\sim 130 \text{ }\mu\text{m}$ thickness were prepared following the above-mentioned process by mixing 90 wt% of the SAC with 5 wt% of CB and 5 wt% of PTFE. A porous glass fiber (Whatman GFB) membrane was used as a separator between them and stainless-steel rods as current collectors. The electrodes and the separator were wetted with a few drops of 6M KOH aqueous electrolyte.

Asymmetric cells of Ni-Co-oxide//SAC were built using four different mass ratios of positive and negative electrodes, *i.e.* 1:1, 1:2, 1:3 and 1:4, respectively in Swagelok™-type two-electrode cells. The active mass of the positive electrode used in all the AAS systems was similar ($\sim 1.20 \text{ mg cm}^{-2}$) and the mass of the negative electrode was modified accordingly. Porous glass fiber was used as separator, stainless steel current collectors, and 6M KOH as an electrolyte. Cyclic Voltammetry (CV), galvanostatic charge-discharge cycling (GC/GD) and electrochemical impedance spectroscopy (EIS) measurements were performed using a multi-channel VMP3 generator from Biologic. For the floating tests the cell voltage was maintained at 1.5 V for 130 hours. Five galvanostatic cycles of charge-discharge were performed every two or five hours to calculate capacity values.

Calculations

Because of the NiCo₂O₄ battery-type positive electrode exhibit non-linear *GD* curves, its specific discharge capacity Q_D (mAh g⁻¹) can be calculated by using the following equation:

$$Q_D = \frac{It_D}{m_{el} 3.6} \quad (1)$$

Where I is the constant current applied, t_D is the time spent during discharge and m_{el} the mass of the electrode.

For the negative electrode containing SAC, the specific capacitance C_D (F g⁻¹) is calculated using the following equation:

$$C_D = \frac{2It_D}{m_{el}U_D} \quad (2)$$

Where I is the constant current applied, t_D is the time spent during discharge, m_{el} is the mass of the electrode and U_D is the voltage difference during discharge.

Since, presence of faradaic positive electrode and non-faradic negative electrode in the asymmetric capacitor produces a non-linear GC/GD curves, the discharge specific capacity Q_D (mAh g⁻¹) of the cell was calculated according to the following equation:

$$Q_D = \frac{It_D}{m_{el} 3.6} \quad (3)$$

Where I is the constant current (A); t_D is the time spent during discharge (s) and m_{el} the mass of both electrodes in an asymmetric cell (g).

The efficiency of non-linear GC/GD can be frequently represented as coulombic efficiency (η_t), calculated by the ratio of integral value of discharge time and charge time.

$$\eta_t = \frac{t_{int,D}}{t_{int,C}} \quad (4)$$

The discharge specific energy density **ED** (W h kg⁻¹) was determined by integrating the area under the GD curve. [38, 39]

$$ED = 0.277 I \int_{t(U_{max})}^{t(U_{min})} U(t) dt / 2 m_{el} \quad (5)$$

where **t(U_{min})** and **t(U_{max})** the time corresponding to the minimum and maximum voltage in the discharge portion of a galvanostatic cycle (s); **U(t)** the instant voltage (V).

The power density **PD** (W kg⁻¹) was calculated according to:

$$PD = ED / 0.2777 [t_D(U_{max}) - t(U_{min})] \quad (6)$$

The values of energy and power density obtained at gradually increasing specific current were used to draw Ragone Plot.

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Keywords: metal oxides, high power, energy storage, hybrid capacitors, aqueous batteries

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Table of Contents

An aqueous asymmetric supercapacitor (AAS) assembled using a nanostructured NiCo_2O_4 as positive electrode and polymer derived super-activated carbon as negative electrode is here proposed. Active materials have been individually characterized and the influence of the electrode mass balance has been investigated. The optimized full cell, built using the 2:1 negative to positive mass ratio, not only enables achieving high energy density at high power density, but more importantly, ensures high cyclability even under harsh floating conditions.