

A review for aqueous electrochemical supercapacitors

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Electrochemical capacitor is the most promising energy-storage device that can meet the demands of high-power supply and long cycle life; however, low-energy density and high-fabrication cost limit its further development. Researchers have paid more attention to the development of electrode material in the past, and very few people attach importance to the research of the electrolyte, especially the redox electrolyte, which is important for improving specific capacitance greatly. This paper presents a review of the research in not only electrode material but also redox aqueous electrolyte and together with an important part of supercapacitor device. The advantages and disadvantages for different electrode material and electrolyte are discussed. And the new trends in supercapacitor development are also summarized.

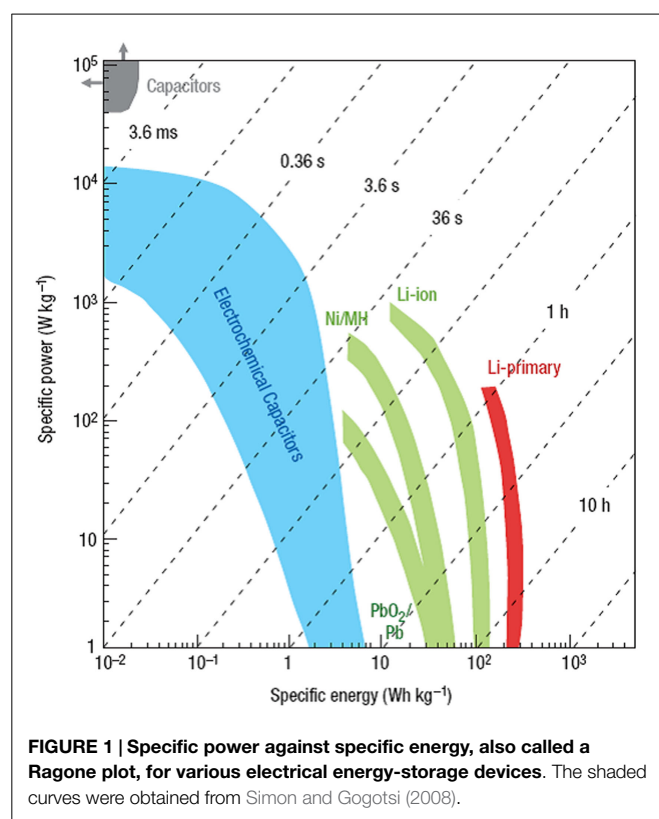
Keywords: electrode, electrolyte, additive, supercapacitor, energy density, power density, cycling stability

Introduction

Energy is an important issue all over the world. The rapid deterioration of environment and depletion of fossil fuels call not only for more clean and renewable energy sources but also more advanced energy conversion/storage systems. Research efforts have mostly focused on two types of electrochemical devices: batteries and capacitors. As shown in **Figure 1** (Simon and Gogotsi, 2008), batteries suffer from low-power density although they have high-energy density, whereas conventional capacitors exhibit high power but low-energy density. Supercapacitor, also known as an electrochemical capacitor (EC), has bridged the gap between battery and conventional capacitor, because of the great advantages including high power and energy supply, long cycle life, flexible operating temperature, and environmental friendliness (Conway, 1999; Burke, 2000, 2010; Frackowiak and Beguin, 2001; Pandolfo and Hollenkamp, 2006; Frackowiak, 2007; Zhang and Chen, 2008; Zhang and Zhao, 2009; Conte, 2010; Inagaki et al., 2010; Zhai et al., 2011; Chen et al., 2013a; Zhi et al., 2013). ECs are widely used in consumer electronics, hybrid vehicles, and industrial power/energy managements. However, the disadvantages of low-energy density and high-fabrication cost for ECs have been identified as a major challenge for the capacitive storage science. To meet the energy demands for practical applications, advanced supercapacitors must be developed with high-energy density without sacrificing the power density and cycle life. The energy density (E) can be obtained by the total capacitance (C) and the cell voltage (V) based on Eq. 1:

$$E = 1/2CV^2 \quad (1)$$

Therefore, there have already appeared two methods in increasing energy density. First, to improve the total capacitance, the most intensive approaches include the discovery of advanced electrode materials and the improved understanding of ion transport mechanism



in small pores (Zhai et al., 2011); however, the improvement in total capacitance is not significant only by electrode materials. Very recently, there have been a few reports that redox additives are introduced into the conventional electrolyte, with additional pseudocapacitive attribution of the additives between the electrode and electrolyte, the capacitance is obviously enhanced (Su et al., 2009; Roldán et al., 2011; Wu et al., 2012; Chen et al., 2013b; Senthilkumar et al., 2013). Second, to improve the cell voltage, asymmetric supercapacitors combining electric double-layer anode and redox reaction cathode show promising capacitive performance.

Electrode Materials

In principle, capacitive behavior can be classified into two types: the electrical double-layer capacitance (EDLC) arising from electrostatic attraction between electrolyte and electrode surface; the pseudocapacitance associated with fast and reversible faradic reactions of the active species on the surface of the electrode (Zhang and Zhao, 2009; Zhai et al., 2011). Therefore, according to the fundamental energy-storage mechanisms, the typical electrode material is EDLC material, such as various carbon materials. The other is pseudocapacitance material based on transition-metal oxides/hydroxides and conducting polymer. Besides, MXenes and MOF material are the latest electrode material.

Carbon Materials

Carbon materials, corresponding to EDLC, are considered the most ideal materials for ECs for high-specific surface area, good

electronic conductivity, excellent chemical stability, easy processing, lower cost, and wide operating temperature range (Zhang et al., 2009a). A variety of carbon materials are involved, such as activated carbon (AC) (Ricketts and Ton-That, 2000; Pognon et al., 2012), carbon aerogels (Saliger et al., 1998; Wei et al., 2005), carbon nanotubes (CNTs), carbon nanofibres (An et al., 2001; Zhang et al., 2009b), and so on. Conventional AC, with a theoretical capacitance of $100 \sim 300 \text{ F g}^{-1}$, exhibits an excellent cycling stability in several electrolytes. Recently, graphene nanosheets, two-dimensional layers of sp^2 -bonded carbon, have been found to be an ideal carbon electrode material for ECs (Stoller et al., 2008; Zhao et al., 2009a; Zhu et al., 2010; Le et al., 2011), with an ideal capacitance of 550 F g^{-1} when the specific surface area of $2675 \text{ m}^2 \text{ g}^{-1}$ is fully used (Liu et al., 2010).

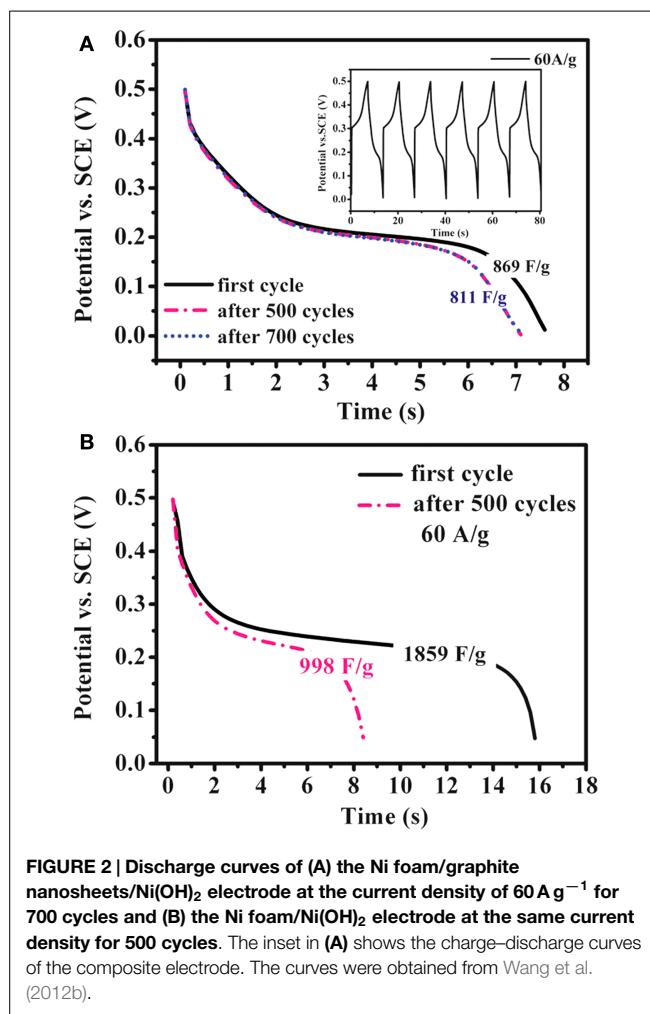
A lot of research has been done for various carbon materials at home and abroad, but the study was only limited to improving the pore size distribution, surface area, and surface functional groups of the carbon material. However, the specific capacitance cannot be improved significantly because of double-layer capacitance mechanisms. At present, the combination of carbon material and pseudocapacitive material can bring synergistic effect, realizing the overall system excellent electrochemical performance.

Metal Oxides/Hydroxides

Based on the faradic pseudocapacitive energy-storage mechanism, metal oxides/hydroxides, such as ruthenium, manganese, cobalt, nickel, and vanadium, can provide higher specific capacitance than conventional carbon materials and better cycling stability than polymer materials.

Ruthenium oxide, with wide potential window, high-redox reversibility and high conductivity shows remarkably high-energy density, power density, and cycling stability (Sakiyama et al., 1993; Jia et al., 1996; Kim and Kim, 2006; Lee et al., 2010). For example, the capacitance can be as high as 1300 F g^{-1} for nanotubular arrayed electrode of hydrous ruthenium oxide (Hu et al., 2006). However, the high cost for precious metal becomes a major barrier for the commercialization. The present study mainly concentrated in two aspects: first, composite ruthenium oxide with carbon or cheap metal oxide material, to improve the utilization ratio of ruthenium oxide; second, seek cheap metal oxide/hydroxide to replace precious metals (Zheng and Jow, 1996; Fang et al., 2001; Hu and Huang, 2001; Jeong and Manthiram, 2001; Ke et al., 2005; Zhao et al., 2012a; Sellam and Hashmi, 2013). For example, Zhang et al. (2014) have reported a facile hydrothermal method without reducer to fabricate graphene-RuO₂ nanocomposites, achieving high-specific capacitance in alkaline/acidic/neutral electrolyte. Wang and Zhang (2004) have designed to load Ru_{1-y}Cr_yO₂ on the TiO₂ nanotubes with a maximum specific capacitance of 1272.5 F g^{-1} obtained. Partially due to the discovery of advanced electrode materials and new synthetic method, more and more electrode materials with high performance have been developed (Simon and Burke, 2008; Simon and Gogotsi, 2008). In recent years, inexpensive pseudocapacitive active materials, such as Co₃O₄/Co(OH)₂ (Simon and Burke, 2008; Wang et al., 2009; Gao et al., 2010; Xu et al., 2010; Yuan et al., 2010, 2012; Anantharamulu et al., 2011; Asano et al., 2011; Xia et al., 2011a; Huang et al., 2012), NiO₄/Ni(OH)₂ (Song and Gao, 2008; Yuan et al., 2009,

2011; Zhang et al., 2010; Cao et al., 2011; Jiang et al., 2011; Xia et al., 2011b; Zhu et al., 2012), MnO_x (Ragupathy et al., 2009; Yan et al., 2010a; Wang et al., 2011; Yu et al., 2011a,b; Lee et al., 2012a, 2013; Song et al., 2012; Si et al., 2013), Fe_3O_4 (Obradovic et al., 2009; Zhao et al., 2009b; Lee et al., 2012b), and so on have attracted the attentions of the researchers. Chang et al. (2010) created nanostructure $\text{Co}(\text{OH})_2$ electrode, exhibiting a high pseudocapacitance of 2800 F g^{-1} and an outstanding rate capability and cyclic stability. Wang et al. have reported a facile synthesis of nickel cobalt layered double hydroxides (LDHs) on conducting Zn_2SnO_4 by CVD and electrochemical deposition. This novel material demonstrates an outstanding electrochemical performance with a high-specific capacitance of 1805 F g^{-1} at 0.5 A g^{-1} , and an excellent rate performance of 1275 F g^{-1} at 100 A g^{-1} (Wang et al., 2012a). Zhao et al. (2011) have prepared layered $\text{Co}(\text{OH})_2$, showing a high-specific capacitance of 651 F g^{-1} , but only 76% of initial capacitance remains after 500 cycles at 50 mV s^{-1} . With higher specific capacitance, the cycling stability of the pseudocapacitive materials has been sacrificed. This drawback must be overcome (Simon and Gogotsi, 2008). To improve low conductivity and poor stability, such inexpensive pseudocapacitive materials are often incorporated into highly conductive nanostructured materials. Recently, composite electrode material has been studied for ECs, showing good electrochemical performance than that of pure oxide/hydroxide. For example, a facile strategy is designed to deposit $\text{Co}(\text{OH})_2$ nanoparticles on graphene sheets in a water-isopropyl alcohol system. The specific capacitance of the graphene/ $\text{Co}(\text{OH})_2$ nanocomposite reaches 972.5 F g^{-1} , leading to a significant improvement compared to each individual counterpart (Chen et al., 2010). Yan et al. (2010b) have composited graphene and Co_3O_4 , exhibiting a high cycle stability (95.6% specific capacitance is retained after 2000 cycles); however, the specific capacitance is only 243.2 F g^{-1} . Unfortunately, most of the reported oxide/graphene materials have been prepared by chemical precipitation method, there exist some problems, the particles are agglomerated easily and a binder is often required, that could decrease the active surface area and increase the internal resistance of the ECs. To overcome the disadvantages, we have focused on binder-free $\text{Ni}(\text{OH})_2/\text{graphene}/\text{Ni foam}$ (Wang et al., 2012b) or $\text{Co}(\text{OH})_2/\text{graphene}/\text{Ni foam}$ (Zhao et al., 2012b) electrode prepared by a combination of PECVD and electrodeposition method, which could be explored as a promising material for ECs because of high-electrochemical activity and cycle stability. From the discharge curves of **Figures 2A,B**, the $\text{Ni}(\text{OH})_2/\text{graphene}/\text{Ni foam}$ electrode maintains 93.3% of the initial specific capacitance after 500 cycles at a high-current density of 60 A g^{-1} , while under the same conditions only 54% specific capacitance retains for the $\text{Ni}(\text{OH})_2/\text{Ni foam}$ electrode, which shows the obvious improvement of cycling stability for the composite electrode (Wang et al., 2012b). In addition, a highly porous $\text{Co}(\text{OH})_2/\text{graphene}$ film on Ni foam has been obtained, as shown in **Figure 3**. The corresponding electrochemical measurement technology also confirmed that the introduction of graphene between $\text{Co}(\text{OH})_2$ and Ni foam demonstrates an obvious enhancement of electrochemical stability compared with $\text{Co}(\text{OH})_2/\text{Ni foam}$ (Zhao et al., 2012b). The excellent pseudocapacitive behavior can be explained to the following (Wang et al., 2012b; Zhao et al., 2012b): (1) graphene can provide high-electrical conductivity and high-specific surface



area, allowing rapid and effective ion charge transfer; (2) $\text{Ni}(\text{OH})_2$ or $\text{Co}(\text{OH})_2$ nanosheets with high-electrochemical activity are directly grown on graphene, with the covalent chemical bonding (C–O–Co or C–O–Ni) formed, favoring the electrochemical stability; (3) graphene has been directly deposited on the Ni-foam collector, can avoid increasing the contact resistance between the electrode and the collector. In order to further improve capacitive properties, the effects of crystallinity and electroconductivity of carbon nanomaterials on $\text{Co}(\text{OH})_2$ are explored (Zhao et al., 2013a). As shown in **Figure 4**, the $\text{Co}(\text{OH})_2$ nanosheet has been electrochemically deposited on graphene nanosheets (GNS) or amorphous carbon (APC). The electrochemical test results are listed in **Table 1**, $\text{Co}(\text{OH})_2/\text{GNS}$ exhibits a high cycling stability, which is due to that the GNS with high conductivity and excellent flexibility can transfer smooth electrons and accommodate the volume expansion/contraction for $\text{Co}(\text{OH})_2$ in the charge–discharge process. By contrast, $\text{Co}(\text{OH})_2/\text{APC}$ shows a high-specific capacitance, which can be ascribed to the lower conductivity for APC, leading to the larger nanosheets of $\text{Co}(\text{OH})_2$, promoting the complete redox reaction of $\text{Co}(\text{OH})_2$ (Zhao et al., 2013a). The carbonaceous supports can not only act as a template to direct the growth of the as-deposited hydroxide but also affect the conductivity of the whole electrode, which may provide a

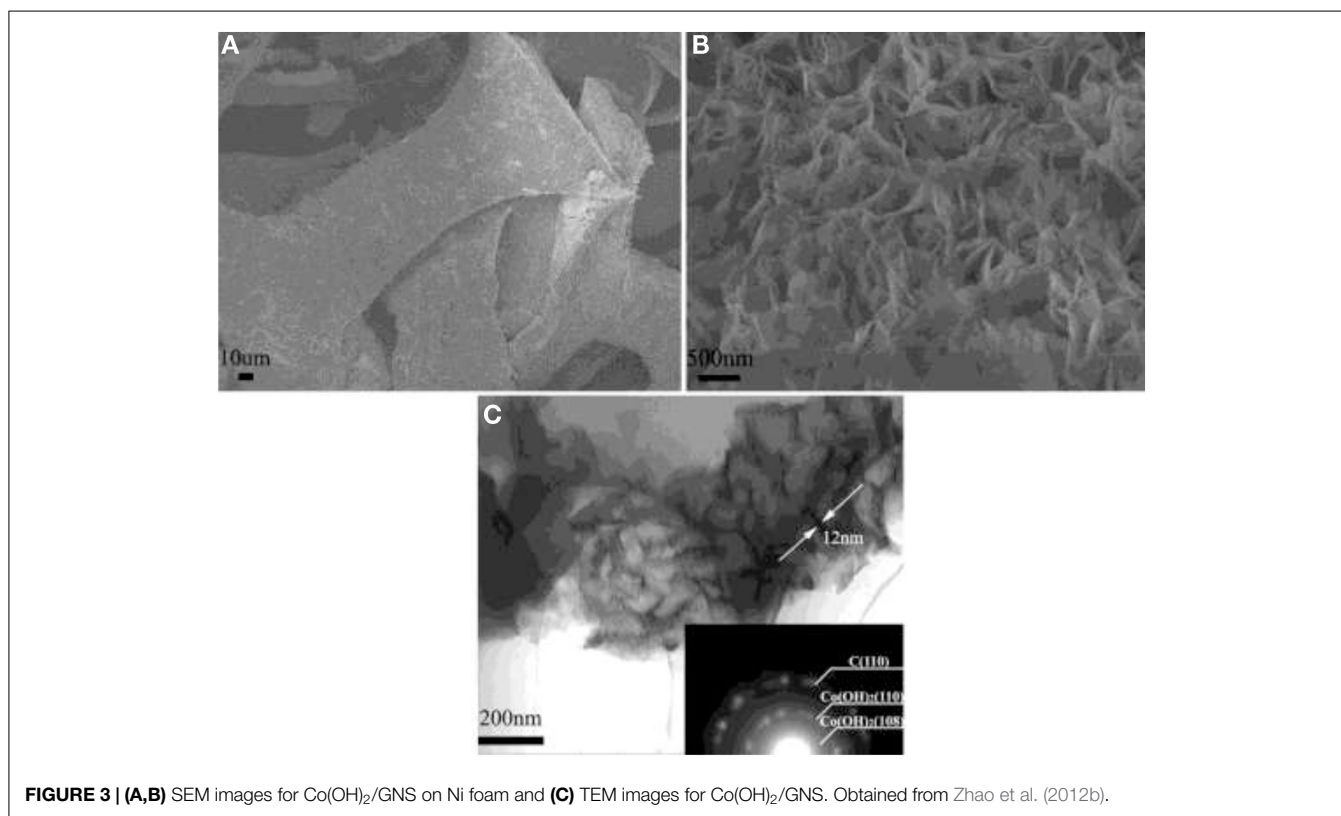


FIGURE 3 | (A,B) SEM images for $\text{Co(OH)}_2/\text{GNS}$ on Ni foam and **(C)** TEM images for $\text{Co(OH)}_2/\text{GNS}$. Obtained from Zhao et al. (2012b).

technical reference for improvement in the pseudocapacitance behaviors and controllable preparation of composite electrode material in the future. Besides hybrid metal oxide with carbon material, a novel hybrid metal oxide core/shell nanowire arrays for ECs has been constructed. For example, Liu et al. choose MnO_2 and Co_3O_4 as the shell and core materials, respectively. The hybrid nanowire array exhibit a high capacitance (480 F g^{-1} at 2.67 A g^{-1}) and good cycle performance (97.3% capacitance retention after 5000 cycles), which is 4–10-fold increase respect to pristine Co_3O_4 array. With this electrode design method, the functions of each pseudocapacitive constituent are effectively utilized, and realize a synergistic effect. Growing from the Co_3O_4 nanowire scaffold directly, the surfaces of MnO_2 nanosheets are well separated, making active material fully available to the Li^+ in the electrolyte. As ultrathin MnO_2 nanosheets construct a highly porous structure on Co_3O_4 nanowire, the Co_3O_4 core nanowires can be accessed by OH^- and initiate the redox reaction (Liu et al., 2011). The concept opens up the possibility of constructing high-performance pseudocapacitive materials without using any carbon-based or conducting media.

Conducting Polymers

Conducting polymers can provide capacitance behavior through the faradic process. When oxidation takes place, ions are transferred to the polymer backbone, and when reduction occurs, the ions are released from this backbone into the electrolyte (Sharma and Bhatti, 2010). Conducting polymers widely used in supercapacitor mainly contain polyaniline (PANI), polythiophene (PTh), polypyrrol (PPy), and their

corresponding derivatives, due to its advantageous properties of low cost, high-voltage window, and high-doping rate during charge–discharge process. However, high resistance and low stability limit the wide application. Especially, swelling and shrinkage may occur during charge–discharge processes, leading to mechanical degradation of the electrodes and fading of the capacitive performance.

Fabricating composite electrode materials to improve the conductivity and stability become the new development direction. For example, a high-performance polyaniline electrode has been prepared by electrochemical deposition on a porous carbon monolith, showing the advancement of high-specific capacitance, excellent rate capability, and good cycling stability. A capacitance value as high as 2200 F g^{-1} is obtained at a current density of 0.67 A g^{-1} , and the specific capacitance is still up to 1270 F g^{-1} even at the high-current density of 66.7 A g^{-1} (Fan et al., 2007). Tao et al. (2014) have developed PPy/ MnO_2 composite through a simple electrodeposition process. The highest areal capacitance of the PPy/ MnO_2 electrode is about 2.45 F cm^{-2} at a current density of 0.2 mA cm^{-2} , and the capacity retention is 98.6% after 1000 cycles.

Latest Electrode Materials

Recently, MXenes have been prepared combining hydrophilic surfaces with good conductivities. MXenes are synthesized by the extraction of the “A” layers from the layered carbides or carbonitrides known as MAX phases. MXenes show promise as electrode materials for Li-ion batteries and Li-ion capacitors; however, many are theoretically predicted (Khazaei et al., 2012;

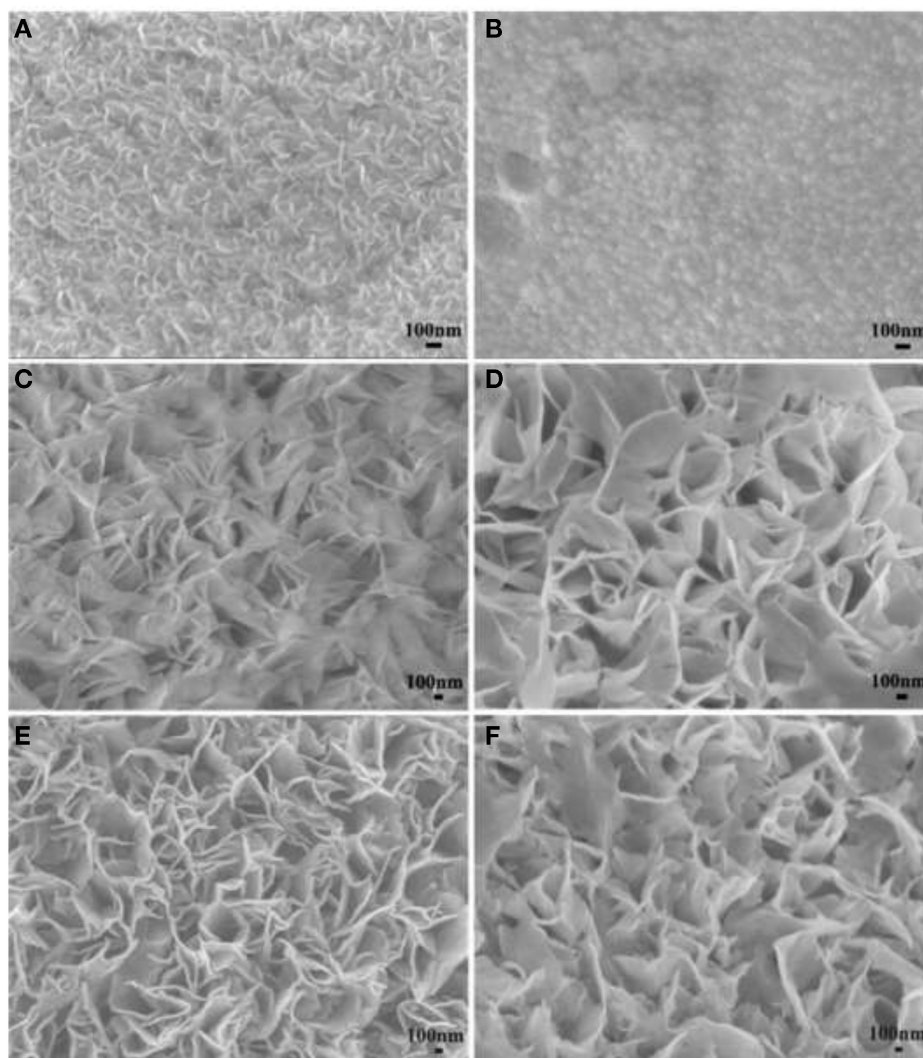


FIGURE 4 | SEM images for (A) GNS, (B) APC, (C) Co(OH)₂/GNS, and (D) Co(OH)₂/APC before discharge/charge cycles; (E) Co(OH)₂/GNS and (F) Co(OH)₂/APC after 2000 discharge/charge cycles. Obtained from Zhao et al. (2013a).

Kurtoglu et al., 2012). Maria et al. have reported an intercalation-induced high capacitances of $\text{Ti}_3\text{C}_2\text{T}_x$ paper electrodes in aqueous electrolytes (KOH or NaOH), 350 F cm^{-1} at 1 A g^{-1} and 60% rate capability from 2 to 100 mV s^{-1} achieved (Lukatskaya et al., 2013). The $\text{Ti}_3\text{C}_2\text{T}_x$ material opens the door for the use of MXenes in energy-storage devices. As noted, the reported capacitances are probably far from the maximum values possible for MXenes in general. A variety of ions should be accommodated between the MXene layers.

Compared to inorganic high-surface-area materials, MOFs offer the theoretical advantage of 100% utilization and improved accessibility of the metal-cation centers due to their regular 3D dispersion in an open structure. For example, the introduction of MOFs in EDLCs has been reported only recently (Diaz et al., 2012; Lee et al., 2012c). Lee et al. have synthesized a Co-based MOF from cobalt nitrate and terephthalic acid, and the capacitive behavior was investigated in various 1M aqueous electrolytes (LiOH, KCl,

LiCl, and KOH). Only in LiOH electrolyte, did the Co-based MOF shows an interesting pseudocapacitive behavior with a specific capacitance of $150 \sim 200 \text{ F g}^{-1}$ and 98.5% capacitance retention after 1000 cycles. However, to date, it is difficult to find that MOFs electrode materials is clear advantaged in performance, durability, or cost compared to other materials. For real breakthroughs, MOFs will probably need to be designed and optimized, with controlling the MOF particle size, improving conductive character, and so on.

Electrolyte

Besides two electrodes, electrolyte plays an important role in capacitor performance, such as ion supplementary, electric charge conduction, and electrode particles adhesive. The requirements for an electrolyte in ES include wide voltage window, high-electrochemical stability, low resistivity, low toxicity, and so on.

TABLE 1 | Electrochemical properties of Co(OH)₂/GNS, Co(OH)₂/APC and Co(OH)₂/GNS-APC.

Active mass	Co(OH) ₂ /GNS	Co(OH) ₂ /APC	Co(OH) ₂ /GNS-APC
Current density			
2 Ag ⁻¹	692.0 Fg ⁻¹	1287.2 Fg⁻¹	784.0 Fg ⁻¹
4 Ag ⁻¹	653.1 Fg ⁻¹	1194.9 Fg ⁻¹	754.9 Fg ⁻¹
8 Ag ⁻¹	610.9 Fg ⁻¹	1051.6 Fg ⁻¹	724.4 Fg ⁻¹
16 Ag ⁻¹	567.3 Fg ⁻¹	904.7 Fg ⁻¹	692.4 Fg ⁻¹
32 Ag ⁻¹	517.8 Fg ⁻¹	762.2 Fg ⁻¹	651.6 Fg ⁻¹
Maintained capacitance 2 ~ 32 Ag ⁻¹	74.8%	59.2%	83.1%
capacitance after 2000 cp at 40 Ag ⁻¹	95.7%	83.8%	93.2%

Bold are the best pseudocapacitive properties including cycling stability, specific capacitance, and rate capability among the three materials, further confirmed that different carbon nanomaterials have different influences on the electrochemical properties of Co(OH)₂.

This table was obtained from Zhao et al. (2013a).

The electrolyte used in ECs mainly includes aqueous electrolyte, organic electrolyte.

Aqueous Electrolytes

As far as the electrolytes are considered, aqueous electrolytes (such as KOH, H₂SO₄, Na₂SO₄ aqueous solution, and so on) have the advantages of high-ionic conductivity, low cost, non-flammability, non-corrosiveness, safety, and convenient assembly in air, compared to organic electrolytes, which are believed to be less conductive, expensive, usually flammable, and higher toxic. However, the potential window (~1.2 V) for aqueous electrolytes is far lower than that of organic electrolyte. According to Eq. 1, low-potential window is the reason of low-energy density that limits its market application. The introduction of redox active substance in aqueous electrolytes can effectively enhance the capacitance via extra redox reaction between the electrode and electrolyte, which is shown in the part of symmetric supercapacitors.

Organic Electrolyte

The restriction of aqueous electrolytes is the limited operating voltage (about 1.2 V). By contrast, organic electrolytes can provide a high-operating voltage up to 4 V. High-potential window is a large advantage for organic electrolyte. Among organic electrolytes solvents, acetonitrile (AN) and propylene carbonate (PC) are the most common. Besides, organic salts such as tetraethylammonium tetrafluoroborate and tetraethylphosphonium tetrafluoroborate have also been used in ECs electrolytes. However, there exist the following problems for organic electrolyte: first, high resistance limits the power density of capacitor; second, high water content limits the working voltage of capacitor.

Supercapacitor

Symmetric Supercapacitors

Symmetric supercapacitors with positive and negative electrode material identical or similar can be divided into electric double-layer capacitor and faradic capacitors according to electrode material working mechanism. Symmetric supercapacitors are

mainly carbon//carbon, Ru//Ru, and cheap metal symmetric supercapacitor.

Electric double-layer capacitor contains carbon material with high-surface area as the electrode material in aqueous or organic electrolytes. Compared to organic electrolytes, aqueous electrolyte is believed to high-ionic conductivity, low cost, and convenient assembly of ECs in air. However, EDLCs only utilize the electrostatic charge at the electrolyte–electrode surface to store electric energy so that the capacitance is limited. Very recently, an effective approach has been reported wherein redox additives are introduced into the conventional electrolyte to enhance the capacitance via extra redox reaction between the electrode and electrolyte. Yu et al. (2012) have doped m-phenylenediamine into a conventional KOH electrolyte for carbon-based ECs. The specific capacitance of the supercapacitor based on the new electrolyte is 78.01 Fg⁻¹, showing an increase of 114.16% over that of a supercapacitor based on a conventional KOH electrolyte. Similarly, Roldán et al. (2011) have reported that via adding electrochemically active compound quinone/hydroquinone (Q/HQ) into the H₂SO₄ electrolyte, an ultrahigh specific capacitance of 5017 Fg⁻¹ achieved for carbon-based EC. The significantly improved capacitance attributes to that the faradaic reactions of the Q/HQ couples (HQ $\xrightleftharpoons{2H^+ 2e^-}$ Q) contribute pseudocapacitance to the electrode. However, working condition is not easily maintained, leading to a poor electrochemical stability. Senthilkumar et al. (2013) have improved the capacitance for AC materials through adding either KI or KBr into 1M H₂SO₄ or Na₂SO₄ electrolyte. With an improved specific capacitance, there is also a problem with the electrochemical stability for only relying on the pseudocapacitive contribution from additive for EDLCs.

Although more attention has been paid to investigating redox electrolyte for enhancing the EDLCs, no any efforts have been done to improve pseudocapacitors. We have aimed at improving the pseudocapacitive behavior of Co(OH)₂/GNS electrode through adding K₃Fe(CN)₆ into KOH electrolyte, in our CV test result, two symmetric anodic/cathodic pairs are superimposed on a broad redox background, corresponding to the redox reaction of Co(OH)₂ electrode and K₃Fe(CN)₆ electrolyte, respectively, indicating that reversible redox reactions of Co(OH)₂ solid electrode and K₃Fe(CN)₆ liquid electrolyte occur simultaneously and independently (Zhao et al., 2013b). The cycling stability for Co(OH)₂/GNS electrode either in KOH electrolyte or K₃Fe(CN)₆ + KOH electrolyte is examined by charge–discharge tests for 2000 cycles at a high current density of 80 Ag⁻¹. Both systems exhibit a high cycling stability, with retention of 94.4 and 91.1% initial capacitance after 2000 cycles. This indicates that the addition of K₃Fe(CN)₆ into KOH electrolyte does not affect the stability of the electrode material. In addition, the system can be charged quickly, and discharged slowly, which means that the promise can be offered to realize a high-performance battery-type supercapacitor.

Although the cost is relatively high, Ru//Ru symmetric supercapacitor shows large specific capacitance, high potential window, and excellent cycling stability. For example, Xia et al. (2014) have developed 1.8 V symmetric supercapacitor using nanocrystalline Ru films as both negative and positive electrodes. The Ru//Ru symmetric supercapacitor exhibits a large areal

TABLE 2 | Electrochemical performance of the asymmetric supercapacitors based on conventional electrode materials.

Electrode	Electrolyte	Capacitance (F g ⁻¹)	Potential window (V)	Energy density (Wh kg ⁻¹)	Power density (kW kg ⁻¹)	Stability	Reference
NaMnO ₂ //AC	Na ₂ SO ₄	38.9	1.9	19.5	0.13	97% (10,000 cp)	Qu et al. (2009)
K _{0.27} MnO ₂ //AC	K ₂ SO ₄	57.7	1.8	25.3	0.14	98% (10,000 cp)	Qu et al. (2010)
NiO//AC	KOH	38	1.5	–	–	50% (1000 cp)	Wang et al. (2008)
MnO ₂ -AC//AC	Na ₂ SO ₄	33.2	2.0	18.2	10.1	92% (2500 cp)	Gao et al. (2011)

TABLE 3 | Electrochemical performance of the asymmetric supercapacitors based on new electrode materials.

Electrode	Electrolyte	Capacitance (F g ⁻¹)	Potential window (V)	Energy density (Wh kg ⁻¹)	Power density (kW kg ⁻¹)	Stability	Reference
rGO//MnO ₂ -rGO	Na ₂ SO ₄	59.9	1.6	21.2	0.82	89.4% (1000 cp)	Wu et al. (2014)
MnO ₂ -NF//G	Na ₂ SO ₄	–	–	30.2	14.5	83.4% (5000 cp)	Gao et al. (2012)
NiCo ₂ O ₄ -Co _{0.33} Ni _{0.67} (OH) ₂ //CMK-3	KOH	87.9	1.6	31.2	396	82% (3000 cp)	Xu et al. (2014)
MnO ₂ -NPG//PPy-NPG	LiClO ₄	193	1.8	86	25	85% (2000 cp)	Hou et al. (2014)
Co(OH) ₂ //VN	KOH	62.4	1.6	22	19.5	80% (4000 cp)	Wang et al. (2014a)
NiO-GF//HPNCNTs	KOH	116	1.4	32	0.7	94% (2000 cp)	Wang et al. (2014b)
CoO-PPy//AC	NaOH	–	1.6	43.5	5.5	91.5% (20,000 cp)	Zhou et al., 2013
NiCo ₂ O ₄ -rGO/AC	KOH	99.4	1.3	23.3	0.32	93% (2500 cp)	Wang et al. (2012c)

capacitance (68 mF cm⁻²), high cycling stability (no capacitance loss after 2000 charge–discharge cycles), and good rate capability. Similarly, a novel symmetric RuO₂/RuO₂ supercapacitor with a high-operating voltage of 1.6 V is also built using the nanocrystalline hydrous RuO₂ electrode, exhibiting an energy density of 18.77 Wh kg⁻¹ at a power density of 500 W kg⁻¹ (Xia et al., 2012).

For other inexpensive transition-metal oxides symmetric capacitors, working potential window are relatively low (no more than 1 V), leading to relatively low-energy density. The researchers try to improve working potential window for the cheap metal oxides symmetric supercapacitor, but the effect is not obvious. For example, Reddy et al. (2009) have synthesized Au–MnO₂/CNT hybrid coaxial nanotube arrays and prepared MnO₂//MnO₂ symmetric capacitor. CNTs serve as an additive for improving the electrical conductivity of the manganese oxide, leading high-specific capacitance, power density, and cycling stability; however, the potential window is only 0.7 V. Lu et al. (2012) have synthesized nickel–cobalt oxide (NCO) nanosheets on FTO substrates and prepared a symmetric supercapacitor based on two NCO electrodes, exhibiting a high-specific capacitance of 89.2 F g⁻¹ at 0.17 A g⁻¹, but a low-potential window of 0.5 V.

Asymmetric Supercapacitors

As an improvement to symmetric supercapacitors, asymmetric supercapacitors combining electric double-layer anode (carbon materials) and redox reaction cathode (such as metal hydroxide/oxide materials, Li-ion battery materials, composite electrode material) show promising capability to enhance the energy density, that is because asymmetric supercapacitors can make full use of the different potential windows of the two electrodes to increase the operation voltage and enhanced specific capacitance in the cell system. More recently, to obtain higher energy density, considerable research efforts have been devoted to the various of asymmetric capacitor systems, mainly including AC//LiMn₂O₄

(Qu et al., 2009, 2010), AC//NiO (Wang et al., 2008), AC//MnO₂ (Gao et al., 2010), and so on. **Table 2** summarizes the electrochemical performances of these conventional asymmetric supercapacitors. For these asymmetric supercapacitors, AC is commonly used as a typical negative electrode material, metal oxides are employed as the positive electrode material. The poor specific capacitance of AC and low stability of metal oxides/hydroxides would also greatly restrict the supercapacitor performance, resulting relatively low-energy density (10 ~ 30 Wh kg⁻¹), power density, and cycling stability. Recently, partially due to the discovery of new electrode materials and new synthesis method, advanced supercapacitors with high performance have been developed. As shown in **Table 3**, asymmetric supercapacitors with high-performance electrode materials as cathode and anode materials show significant superiority in energy density (~90 Wh kg⁻¹), power density, and cycling stability.

Trends in ES

Electrochemical capacitors with high-power density and cycling performance have bridged the gap between conventional capacitors and batteries. However, one of the key challenges for ES is the limited energy density. To overcome this challenge, ECs research should focus on improving the specific capacitance and widen potential window.

- (1) Improve the specific capacitance. One common strategy is to design and synthesis new materials, which must satisfy the following conditions: first, good conductivity for efficient charge transport; second, high-specific surface area for more active sites; third, good mechanical and electrochemical stability for good cycling performance; last, favorable pores-size distribution for high-rate ions diffusion. The ECs electrode material exploration directions are composite materials and nanomaterials, with coating active materials with conductive

carbon or constructing a novel hybrid metal oxide nanostructure electrode for ECs. Nanocomposite can realize synergistic effect, facilitating electron and proton conduction, enhancing specific surface area, expanding active sites, inducing porosity, protecting active materials from mechanical degradation, improving cycling stability. Another effective one is to pursue new electrolyte with high-electrochemical activity and reversibility, contributing additional pseudocapacitance in specific potential window, and the problem of electrochemical stability for the composite electrode system should be paid more attention further.

- (2) Widen the potential window. The strategy of developing and matching asymmetric capacitors can make use of the different potential windows of the two electrodes to increase the operation voltage in the cell system. However, the matching problem appears between positive and negative electrode. If the electrodes are matched well, the overall performance of the supercapacitor will be improved. Otherwise, its performance may drop or the supercapacitor may be damaged.

Solid-state supercapacitors (SSCs) are emerging as energy-storage devices due to excellent stability, light weight, and easy to handle, however, suffer from poor rate capability due to limited

ion-diffusion rate in solid-state electrolytes, large resistance of the electrode material. Asymmetric capacitors with redox electrolyte can exhibit large specific capacitance and wide potential window, resulting in an enhanced energy density. The supercapacitor can be regarded as a novel hybrid supercapacitor application that combines two energy-storage processes: the double-layer capacitance or faradaic pseudocapacitance characteristic from electrode materials and the faradaic pseudocapacitance from electrolyte. It is important to design high-performance electrode materials, choose the suitable electrolyte, solve well matching problem. With the high resistance and low charge-discharge stability resolved, such asymmetric supercapacitor is expected to be a highly promising candidate for application in high-performance energy-storage systems.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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