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# Electrochemical Capacitor Performance: Influence of Aqueous Electrolytes

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Additional information is available at the end of the chapter

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## Abstract

Due to low energy characteristics such as energy density and cyclic life, it is mandatory to enhance the energy characteristics of the supercapacitors (ESs). Electrolytes have been recognized as the most prominent ingredients in electrochemical supercapacitor performance. Most commercially available ESs use organic electrolytes and have some advantage like wide operating voltage. However, compared with aqueous alternatives, organic electrolytes are expensive, flammable, and, in some cases, toxic. It is reliable to assert that even though aqueous electrolytes examined by a cramped working voltage, the ions present in them are yet capable of incredibly faster carrier rates than organic electrolytes and can achieve better performance of ESs. Thus, efforts turned toward enlarging the working voltage window of aqueous electrolytes to increase overall operating potential and energy density of supercapacitor devices. This book chapter comprises the latest accomplishments in this area and provides an insight into the aqueous electrolyte advancement.

**Keywords:** supercapacitors, energy density, aqueous electrolyte, operating voltage, electrolyte

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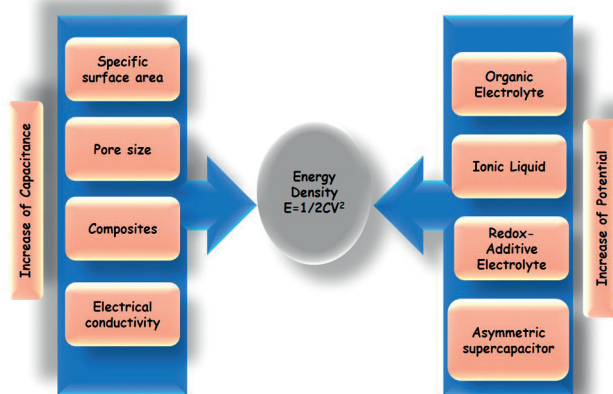
## 1. Introduction

The dramatic global warming and the accessibility to fossil fuels in the earth require society to shift in the direction of renewable and sustainable resources. Due to this, the growth and ramp-up of sustainable, clean energy sources, as well as their associated technologies, are taken into account worldwide as a critical problem. The majority of the renewable and clean energy sources depend on the countrywide weather conditions. Among different energy storage systems, the electrochemical energy storage (EES) systems including batteries, fuel cells, as well as electrochemical capacitors or supercapacitors (ESs) are most efficient and frequently used in several applications [1]. The most common characteristic of these three

devices is that the energy-producing processes perform at electrode/electrolyte interfaces. In both academia and industry, supercapacitors have drawn much importance due to benefits of high power density and long cyclic life compared with batteries and fuel cells [2]. By their charge storage process, ES is divided into three categories: (1) electric double layer capacitors (EDLC), (2) pseudocapacitors, and (3) hybrid capacitors [3]. Due to the technical maturity of EDLCs, almost all of the commercially available supercapacitors are made up by using EDLC electrode materials such as activated carbon. The low energy density ( $\sim 10 \text{ Wh kg}^{-1}$  for commercial supercapacitors) is truly the most significant challenge for supercapacitors in comparison to rechargeable batteries and fuel cells [4]. For that reason, enormous research attempts were carried out aiming to enhance the energy density of supercapacitors [5]. The important characteristic to get extraordinary energy density of supercapacitors is shown in **Figure 1**. As seen from the figure, the energy density of supercapacitors is directly proportional to the capacitance and square of the working voltage. Therefore, enhancing the capacitance and improving the working potential are considered as promising approaches to further improve high energy density supercapacitors. The high energy density can be attained by choosing appropriate electrode material with a high specific capacitance and electrolyte with a large operating voltage. Considering that the energy density is directly proportional to the square of the voltage, increasing the working potential window could be a more efficient way to improve the energy density rather than to improve the specific capacitance. Therefore, developing a new electrolyte with a large potential window is the top priority effort in comparison to seeking new electrode materials.

### 1.1. Effect of the electrolyte on supercapacitor performance

It is well recognized that the working potential of the supercapacitors is highly relying on the electrochemical stability of the electrolytes. For example, organic electrolytes and ionic liquid (IL)-derived supercapacitors can easily be handled at a large potential window of 2.5–2.7 and 3.5–4.0 V, respectively [6]. However, the electrodes are steady in aqueous electrolytes within the potential choice of 1.0–1.3 V due to  $\text{H}_2/\text{O}_2$  evaluation reactions [7]. Since the interaction involving the electrode and electrolyte acts an essential function in the overall supercapacitor



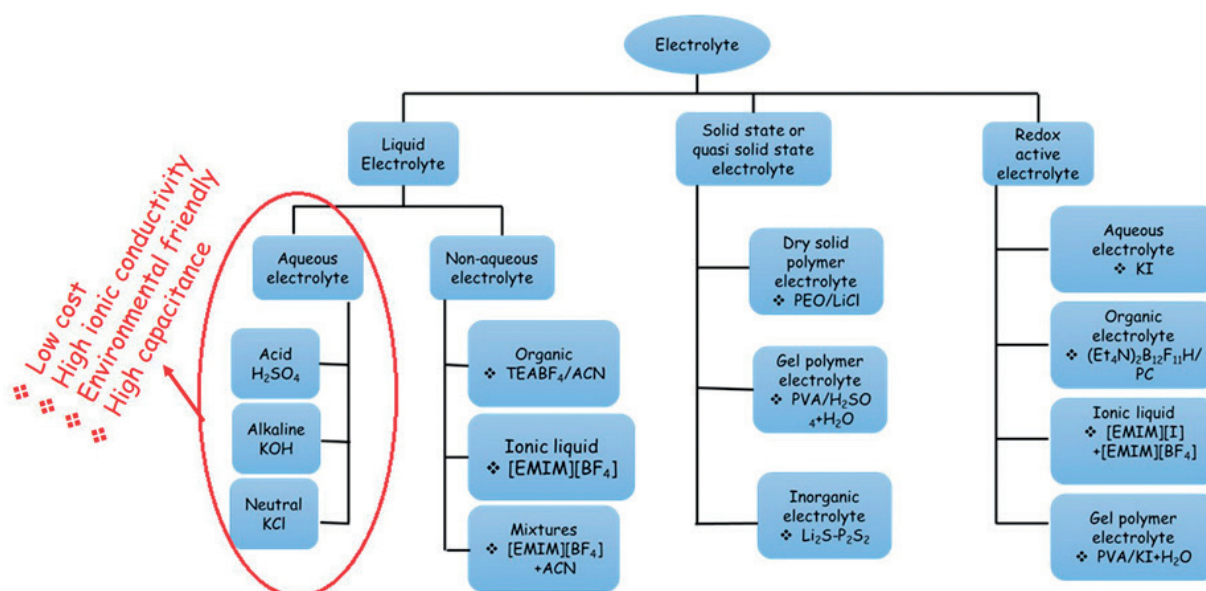
**Figure 1.** Important characteristic of high energy density supercapacitors.

performance, aside from the operating voltage, the electrolytes have substantially influenced on the other parameters such as power density, cycling stability, operating temperature, equivalent series resistance, life time, and self-discharge rate of the capacitors [8]. The electrolyte ionic conductivity performs a serious role in the internal resistance of supercapacitors. It is highly crucial that the electrolyte ion size should be equal or less than that of the pore size of electrode material to possess a high capacitance and a high power density [9]. For a few cases, the freezing point and viscosity of electrolytes also affect the thermal stability of supercapacitor performance, and hence the working voltage range would be shifted [10, 11].

An ideal electrolyte of supercapacitor needs to have some fundamental requirements: (1) broad potential window, (2) a wide range of working temperature, (3) high ionic conductivity, (4) low viscosity, (5) high electrochemical stability, (6) environmentally friendly, (7) low cost, and (8) low flammability. Each electrolyte has its merits and drawbacks, and it is feasible to meet all the above specifications with one electrolyte. Nonstop and tremendous research efforts have been made in the present and will also keep going in the future for the electrolyte development investigation.

## 2. Types of electrolyte

Following the nature of electrolyte like the ion type, ion size, ion concentration, and the interplay among the ion and solvent, various electrolytes have been developed and examined currently. The electrolyte can be divided into three groups such as liquid, solid or semisolid, and redox-additive as shown in **Figure 2**. The liquid electrolyte can be further classified into aqueous electrolyte, nonaqueous electrolyte, and organic electrolyte [12].



**Figure 2.** Classification of supercapacitor electrolytes.

As mentioned previously, no single electrolyte can meet all the requirements. For example, both high capacitance and ionic conductivity can be achieved by aqueous electrolytes, but the narrow decomposition voltage made the lower operating voltage of aqueous electrolytes. Though organic and ionic liquid electrolytes provide a wide operating voltage, they normally suffered from the low conductivity (large internal resistance), high cost, and high flammability which cause continual trouble during application in supercapacitor device. In this regard, extensive efforts are committed to the successful development of the overall performance of electrolytes. Some strategies have already been strived to enhance the electrolyte performance, including “(1) developing an entirely new electrolyte as well as improving its efficiency concerning a wide range of functioning voltage, high ionic conductivity, large working temperature range, and so on [13]; (2) investigation of the effect of electrolytes on capacitance, energy and power densities, thermal stability, and self-discharge rate of supercapacitors [14]; and (3) initiate and becoming familiar with a fundamental concept of the electrolyte on supercapacitor performance over sophisticated characterization, modeling, and simulation utilities [15].”

3. Aqueous electrolytes

Usually, regarding the energy density study, the aqueous electrolytes really are a poor selection for technical supercapacitor products because of their small voltage window. This could be the reason for why nearly all the commercial supercapacitors use organic electrolyte rather than aqueous electrolytes. Though aqueous electrolytes possess an insufficient cell voltage, they were considerably employed in the literature from 1997 onward because of that aqueous electrolytes seem to be cheaper and can be quite easily taken care of in the laboratory without having a special circumstance. However, ionic liquid and organic electrolytes generally call for complex purification treatments under a rigidly controlled environment to stay clear of moisture. All of these features of aqueous electrolytes tremendously explain the design and assembling of supercapacitors. Generally, aqueous electrolytes exhibit extremely high conductivity (**Table 1**) which is at least one magnitude larger than that of organic or IL electrolytes.

Electrolyte	Conductivity (mS cm <sup>-1</sup> )	Potential window (V)
Aqueous KOH	540	0–1
Aqueous KCl	210	0–1
Aqueous H <sub>2</sub> SO <sub>4</sub>	750	0–1
Aqueous K <sub>2</sub> SO <sub>4</sub>	88.6	0–1
Aqueous Na <sub>2</sub> SO <sub>4</sub>	91.1	0–1
Organic TEABF <sub>4</sub> /PC	14.5	2.5–3
Organic TEABF <sub>4</sub> /ACN	59.9	2.5–3
IL, [Et <sub>2</sub> MEIM] <sup>+</sup> [BF <sub>4</sub> ] <sup>-</sup>	8	4

**Table 1.** Electrolytic conductivity and operating voltage of various electrolytes at room temperature.

The high conductivity of the aqueous electrolyte is propitious for reducing equivalent series resistance (ESR) which leads to significantly high power density supercapacitors.

To evaluate the overall performance of aqueous electrolytes, some typical criteria should be taken into consideration such as the dimensions of hydrated and bare ions (**Table 2**), the flow of ions which alters the ionic conductivity, as well as the specific capacitance.

The aqueous electrolytes can be categorized into three groups such as alkaline, acid, and neutral solutions. The most commonly used aqueous electrolytes are KOH,  $\text{H}_2\text{SO}_4$ , and  $\text{Na}_2\text{SO}_4$ , respectively.

### 3.1. Acid electrolytes

Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is the most frequently used aqueous acid electrolyte in supercapacitor simply because of its extremely high conductivity ( $\sim 0.8 \text{ cm}^{-1}$  at  $25^\circ\text{C}$  for 1 M  $\text{H}_2\text{SO}_4$ ) [16]. Since the electrolyte ionic conductivity is dependent on the concentrations, optimum molar concentrations have already been investigated to attain the highest possible ionic conductivities of a given electrolyte at particular temperature. So far, the electrolyte ionic conductivity can be quickly dropped when the concentration becomes extremely low or excessively high. So, the greater number of research studies uses 1 M  $\text{H}_2\text{SO}_4$  solution, especially for carbon-based supercapacitors.

Type of ion	Size of bare ion (Å)	Size of hydrated ions (Å)	Gibbs energy (kcal mol <sup>-1</sup> )	Ion conductivity (S cm <sup>2</sup> mol <sup>-1</sup> )
H <sup>+</sup>	1.15	2.80		350.1
Li <sup>+</sup>	0.60	3.82	138.4	38.69
Na <sup>+</sup>	0.95	3.58	162.3	50.11
K <sup>+</sup>	1.33	3.31	179.9	73.5
NH <sub>4</sub> <sup>+</sup>	1.48	3.31	–	73.7
Mg <sub>2</sub> <sup>+</sup>	0.72	4.28	–	106.12
Ca <sub>2</sub> <sup>+</sup>	1.00	4.12	–	119
Ba <sub>2</sub> <sup>+</sup>	1.35	4.04	–	127.8
Cl <sup>-</sup>	1.81	3.32	–	76.31
NO <sub>3</sub> <sup>-</sup>	2.64	3.35	–	71.42
SO <sub>4</sub> <sup>2-</sup>	2.90	3.79	–	160.0
OH <sup>-</sup>	1.76	3.00	–	198
ClO <sub>4</sub> <sup>-</sup>	2.92	3.38	–	67.3
PO <sub>4</sub> <sup>3-</sup>	2.23	3.39	–	207
CO <sub>3</sub> <sup>2-</sup>	2.66	3.94	–	138.6

**Table 2.** Size of electrolytic bare and hydrated ions and their conductivity [10].



### 3.1.1. $H_2SO_4$ electrolyte-based EDLC and pseudocapacitors

Recently, several researchers discovered that for the carbon-based capacitors (EDLCs), specific capacitance obtained in the  $H_2SO_4$  electrolyte is much higher than the specific capacitance in a neutral electrolyte. Moreover, due to the high value of  $H_2SO_4$  ionic conductivity, the ESR value of supercapacitors is much lower in comparison to the neutral electrolyte. Torchala et al. have examined the EDLC behavior of activated carbon in the  $H_2SO_4$  electrolyte, and they ascertained that the specific capacitance could be raised with increased electrolyte conductivity [17]. In past several years, many literatures have reported that the carbon-based materials had provided the specific capacitance within the range between 100 and 300 F g<sup>-1</sup>. Certain reported values are usually higher compared to those acquired in the commercial electrolytes. The changes in specific capacitance might replicate the diverse interplays among the electrode materials and the electrolyte ions caused by various electrolytes. As pointed out above, because of the small potential window of aqueous electrolyte, the energy density of EDLCs turns considerably lower. Thus, enormous attempts have been performed to raise the ES energy density by investigating other methods which can include utilizing pseudocapacitive behavior in electrodes.

In addition to the EDLC capacitance, it was discovered that the  $H_2SO_4$  electrolyte also induced pseudocapacitance contribution due to the active redox reactions of carbon material surface functionalities. Introducing some heteroatoms that include nitrogen, oxygen, and boron to the carbon materials surface could enhance the pseudocapacitance contributions [18]. The doping of heteroatoms not only increases the specific capacitance but also improves the cycle life of the electrode materials even at a larger potential in the aqueous electrolytes. The pseudocapacitance materials including metal oxides, metal sulfides, and conducting polymers have much higher theoretical capacitance value compared to carbon-based electrodes in aqueous electrolyte [19]. Since the metal oxides and sulfide materials are highly sensitive to nature and pH of the electrolyte, these electrodes typically are not steady in the acidic electrolyte which restricts use in commercial products. As well known, ruthenium oxide ( $RuO_2$ ) is one of the potential electrodes that has been extensively examined for its pseudocapacitance in the  $H_2SO_4$  electrolyte. Amorphous  $RuO_2$  can deliver a very high value of ~1000 F g<sup>-1</sup> in acidic electrolyte resulting from easy insertion of the proton in the amorphous structure. Sadly, the expensive and limited Ru sources have restricted their practical usage.

### 3.1.2. $H_2SO_4$ electrolyte-based hybrid supercapacitors

To increase the energy densities of supercapacitors in aqueous electrolytes, designing a hybrid supercapacitor is the most potentially promising way. As a result of the gas evolution reactions, the maximum cell voltage is limited for a symmetric supercapacitor by using the same electrode materials in aqueous electrolyte. The combinations of two alternative electrodes (asymmetric supercapacitors) can be performed in different working potentials, leading to a larger functioning potential window in aqueous electrolyte. Currently, several types of asymmetric-based supercapacitors such as carbon// $PbO$ , carbon// $RuO_2$ , and carbon with various mass and properties in cathode and anode electrodes have already been examined in strong acidic electrolytes. An energy density of 25–30 Whkg<sup>-1</sup> has been delivered by carbon// $PbO_2$  asymmetric supercapacitor, which was considerably higher than that of the symmetric

carbon-based EDLCs ( $3\text{--}6\text{ Whkg}^{-1}$ ) in the acidic electrolyte. Similar to metal oxide, conducting polymer and carbon-based asymmetric supercapacitor have delivered enough energy density for commercial applications. It was found that the energy density could reach up to  $11.46\text{ Whkg}^{-1}$  when polyaniline (PANI) was used as a positive electrode and carbon as a negative electrode at a wider potential range ( $-1\text{ V}$  to  $+1\text{ V}$ ) [20]. Though the energy density has reached higher than symmetric carbon capacitors, PANI is limited in the commercial product due to its poor stability. The stability can be improved through the use of liquid  $\text{H}_2\text{SO}_4$  electrolyte for conducting polymer-based electrodes. When compared to solid-state polymer aqueous electrolytes, the thermal stability of liquid  $\text{H}_2\text{SO}_4$  is high. Thus, the stability and the energy density of supercapacitors could possibly be improved in liquid-based electrolytes. For example,  $0.5\text{ M H}_2\text{SO}_4$  liquid electrolyte has delivered the energy density about  $\sim 20\text{ Wh kg}^{-1}$  for  $\text{RuO}_2$ /carbon nano-onion symmetric ESs, which is twofold higher than that of polymer gel acidic electrolyte (Figure 3) [21].

### 3.2. Alkaline electrolytes

Since acidic electrolytes are commonly not suitable for some cost-effective metal materials and metal oxides (Ni, Co, Eu, etc.), alkaline electrolytes have been utilized extensively in the literatures. Potassium hydroxide (KOH) is most commonly used alkaline aqueous electrolyte, simply because of its significantly better ionic conductivity ( $0.6\text{ S cm}^{-1}$ ).

#### 3.2.1. Alkaline electrolyte-based EDLC and pseudocapacitors

The energy density of EDLC-based supercapacitors in aqueous KOH is similar to that reported with  $\text{H}_2\text{SO}_4$  electrolyte. So, massive efforts have been given to raise the EDLC material

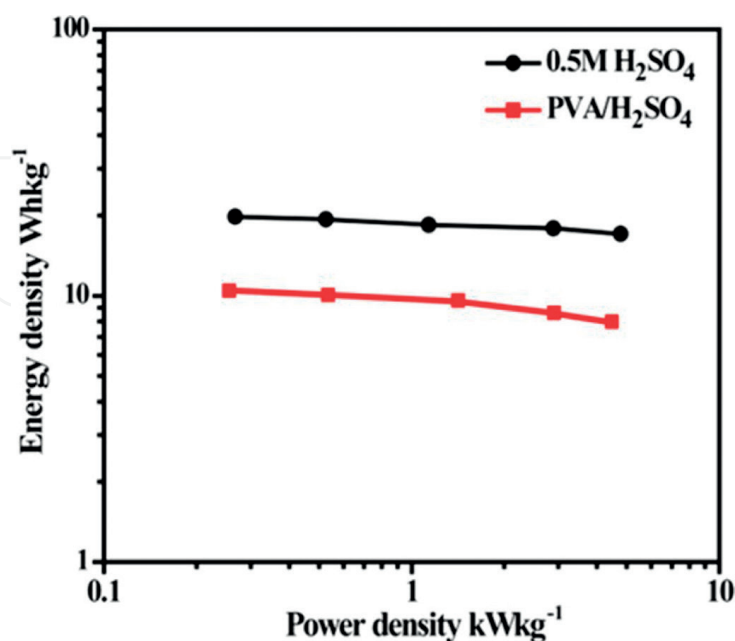
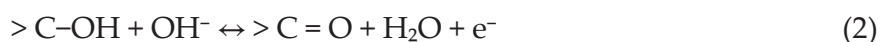
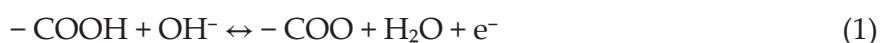


Figure 3. Ragone plot of  $\text{RuO}_2$ /carbon nano-onion symmetric ESs. (Reproduced from [21] with permission from ACS).



energy density in the alkaline electrolyte by increasing the capacitance and enhancing the operating voltage. Some of the efforts were made as follows: (1) increasing carbon materials' specific capacitance by doping some pseudocapacitance functional groups, (2) discovering some pseudocapacitance materials with large specific capacitance, (3) establishing new composite materials (EDLC material + pseudocapacitance material), and (4) developing asymmetric supercapacitors with a wider potential window.

As pointed out previously, the functional groups of carbon materials undergo the faradic redox reactions which are due to the interaction involving the electrolyte ions and the attached functional groups. It has been confirmed in literatures that the KOH electrolyte was favorable for the functioning/doping carbon materials to further increase their pseudocapacitance. The existence of oxygen functional groups in carbon material (graphene) can increase the pseudocapacitance contribution in KOH electrolyte, and hence overall capacitance of the electrode can be improved [22]. The redox reaction of those functional groups in KOH electrolyte can be expressed as follows:



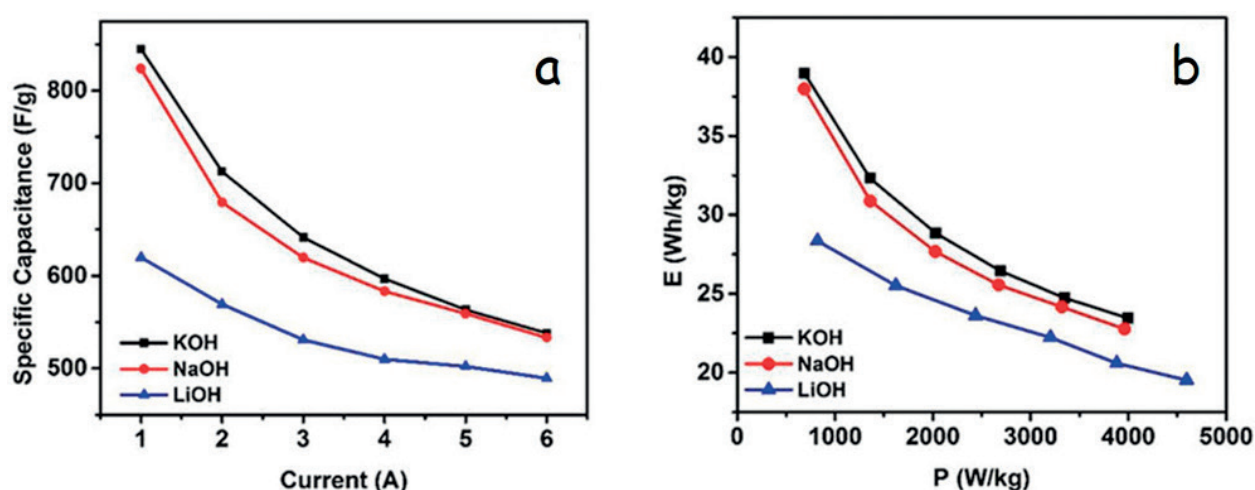
From this, it is well known that the electrode and electrolyte ion interaction performs a serious role for pseudocapacitance contribution. Since the theoretical capacitance of some metal oxides, sulfides, and hydroxides such as  $\text{Co}_3\text{O}_4$ ,  $\text{NiO}$ ,  $\text{MnO}_2$ ,  $\text{NiCo}_2\text{O}_4$ ,  $\text{Ni}(\text{OH})_2$ ,  $\text{CoS}$ , etc. have extremely high values, these electrode materials have also been examined for supercapacitor applications in aqueous KOH electrolyte. For example, the specific capacitance has reached extremely high ( $\sim 1400 \text{ F g}^{-1}$ ) for  $\text{Co}_3\text{O}_4$  nanofilm in 2 M KOH electrolyte [23]. The conversation of different oxidation states like  $\text{Co}^{\text{II}}$  to  $\text{Co}^{\text{III}}$  and then  $\text{Co}^{\text{IV}}$  in KOH aqueous electrolyte enhanced the capacitance of the electrode and described as follows:



Similarly, though metal sulfides ( $\text{CoS}$ ,  $\text{MnS}$ ,  $\text{NiS}$ , etc.) have poor pseudocapacitance performance in KOH electrolyte, the electrochemical transformation of sulfides into some different electroactive forms ( $\text{Co}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_2$ ) might improve the pseudocapacitance of the electrodes. Some characteristics of the electrolyte including ion type, size, and concentrations can affect the working temperature and ES performance. Since the pH of KOH electrolyte seems to be high, the corrosion of electrode surface might be possible when using more concentrated electrolyte. Thus, optimization of the electrolyte concentration is a mandatory task to avoid the corrosion behavior of current collector. In addition to the concentration, the electrolyte ion type and size also impact the total efficiency of ESs. The rate of intercalation/de-intercalation of the ions in the electrolyte can determine the quantity of pseudocapacitance of materials.

Misonn et al. [24] have achieved a higher specific capacitance of  $\text{MnO}_2$  electrode in LiOH electrolyte than that in KOH, resulting from the miniature-sized ionic radius of  $\text{Li}^+$  ions. The smaller radius can be favorable to the relatively easy intercalation/de-intercalation of ions into electrode material and improved the redox reactions. In addition, the effects of the different aqueous electrolytes on  $\text{NiCo}_2\text{O}_4$  nanostructures at a wider range of temperature have been investigated, and the highest energy density from KOH electrolyte has been achieved in comparison with NaOH as well as LiOH electrolytes (**Figure 4**). Because of the smaller size of  $\text{K}^+$ , the ion mobility in KOH turned into much higher which enhances the fast redox reactions between electrode and electrolyte [25]. Barzegar also reported that for activated carbon electrode, 6 M KOH could demonstrate significantly better electrochemical performance than  $\text{Na}_2\text{SO}_4$  and LiCl electrolytes [26]. Besides of the cations, electrolyte anions also play a crucial role in ES performance. Ramachandran et al. performed extensive research toward the effect of anions on the specific capacitance behavior in potassium-based alkaline and neutral electrolytes (KOH and KCl) [27]. They have reported that the small size of  $\text{OH}^-$  ions can enhance the redox reaction of cobalt sulfide/graphene materials in KOH electrolyte. Due to the smaller ionic size of  $\text{OH}^-$ , only a limited number of literatures are available for comparative studies of different alkaline aqueous electrolyte behaviors, and still the electrolyte phenomenon and mechanisms are unclear.

It is well known that the cyclic stability of pseudocapacitive materials is generally poor in the alkaline electrolyte when compared to EDLC materials, which could be associated with the repeated redox reactions in the electrolyte. An existing research was focused on enhancing the cyclic life of pseudocapacitive materials with carbon materials (composite materials). The composite materials not only improved the electrode stability but also increased the working potential range of alkaline electrolytes. For example,  $\text{Fe}_2\text{O}_3$  nanodots/N-doped graphene composite material showed the ultralong cyclic stability of 75.3% even after 100,000 cycles in KOH electrolyte [28], and this might be due to the fact that the pyrolic N atoms in graphene can promote the electron transfer reactions of the composite.



**Figure 4.** (a) Specific capacitance plot and (b) Ragone plot of  $\text{NiCo}_2\text{O}_4$  at various alkaline aqueous electrolytes. (Reproduced from [25] with permission from Nature).

### 3.2.2. Alkaline electrolyte-based hybrid supercapacitors

A sequence of alkaline electrolytes has been studied for hybrid supercapacitors to increase their energy density with a wide range of the potential. The working voltage of the KOH electrolyte can be improved up to  $\sim 1.7$  V when asymmetric electrodes are used. For example, carbon//metal hydroxides (carbon//Ni(OH)<sub>2</sub>  $\sim 1.7$  V and carbon//Co(OH)<sub>2</sub>  $\sim 1.6$  V) and carbon//RuO<sub>2</sub> ( $\sim 1.4$  V) asymmetric devices have been delivered high energy densities in KOH electrolyte. As a result of their wider potential window and high faradic reactions, most of the hybrid devices could deliver higher energy densities between 20 and 40 W h kg<sup>-1</sup>, which has been similar to rechargeable lithium-ion batteries. Recently, Chen and Xue [29] have demonstrated that the vanadium-based colloids/activated carbon-based hybrids could provide a high energy density of  $\sim 50.4$  W h kg<sup>-1</sup> with potential range of 0–1.8 V in 2 M KOH electrolyte. In situ formation of electroactive vanadium-based colloids with high utilization of cations in asymmetric device enhanced the performance and the operating voltage. Thus, developing asymmetric hybrid supercapacitor is an efficient way to increase the operating voltage and could be used in practical applications in KOH electrolyte.

### 3.3. Neutral electrolyte

When compared with alkaline and acid electrolytes, neutral electrolytes have also been studied extensively due to their larger working potential and less corrosive feature. Up to date, there are many types of neutral electrolytes such as LiCl, Li<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaCl, KCl, K<sub>2</sub>SO<sub>4</sub>, etc. used in supercapacitor studies. Among them, Na<sub>2</sub>SO<sub>4</sub> neutral electrolyte has shown promising electrochemical reactions for electrodes especially pseudocapacitance materials.

#### 3.3.1. Neutral electrolyte-based EDLC and pseudocapacitors

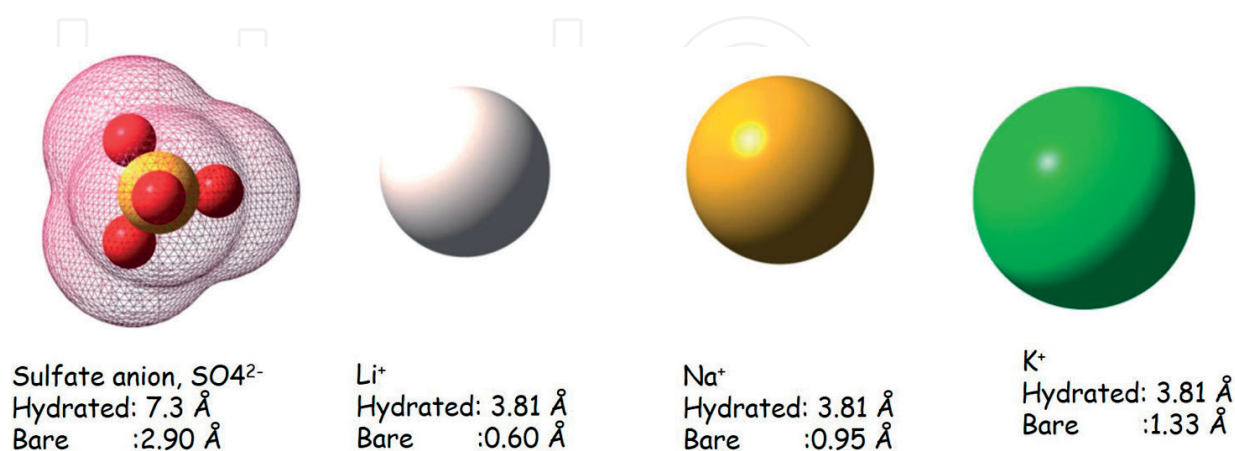
Since the lower H<sup>+</sup> and OH<sup>-</sup> concentrations of the neutral electrolyte, the potential of hydrogen and oxygen evolution reaction can be shifted into the higher potential window and the electrolyte-stable potential windows (ESPW) can be increased in comparison to the alkaline electrolyte. Demarconnay et al. reported an excellent cyclic stability even after 10,000 charge-discharge cycles for the symmetric-activated carbon-based device at a high cell potential of 1.6 V in 0.5 M Na<sub>2</sub>SO<sub>4</sub> neutral electrolyte [30]. The cell voltage can be extended up to 2.2 V for carbon-based electrodes in the Li<sub>2</sub>SO<sub>4</sub> electrolyte as a consequence of its miniature size of bare ions (**Table 2**). The small size of Li<sup>+</sup> ions can enhance the charge accumulation process in carbon electrode/electrolyte interfaces and avoid the evolution of gases such as oxygen and hydrogen at higher potential. The reported operating voltage of neutral electrolyte for carbon materials is relatively higher and less corrosive than H<sub>2</sub>SO<sub>4</sub> and KOH electrolytes. Symmetric carbon ESs in neutral electrolyte have been identified as a potential candidate for higher energy density and lower environmental impact devices. A few comparable studies of the neutral electrolyte with various salts (Li<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>) based on carbon ESs have been reported to experience the impact of ions on capacitive performance. Several studies reported the electrochemical performance of carbon materials shown in neutral electrolytes following the order Li<sub>2</sub>SO<sub>4</sub> > Na<sub>2</sub>SO<sub>4</sub> > K<sub>2</sub>SO<sub>4</sub> [31, 32]. As mentioned above, the performance of ESs not only relies

on the type of electrolyte but also depends on the electrode preparation and analysis circumstances, which include voltage, scan rate, and temperature. With this view, the additional research work may be required to interpret the effect of salts on the ES performance.

Some of the pseudocapacitive materials like  $\text{RuO}_2$ ,  $\text{MnO}_2$ , and  $\text{V}_2\text{O}_5$  have shown excellent ES performance in neutral electrolytes.  $\text{MnO}_2$  is the most common pseudocapacitive material, and it has been studied widely in the neutral electrolyte. Li et al. [33] have confirmed that the order of energy density and specific capacitance of mesoporous  $\text{MnO}_2$  electrode is obtained in neutral electrolytes as follows:  $\text{Li}_2\text{SO}_4 > \text{Na}_2\text{SO}_4 > \text{K}_2\text{SO}_4$ . This behavior appears to be associated with the magnitude of these alkali metal bare and hydrated ion size, i.e.,  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ , suggesting that the smaller ion size is advantageous for improving the performance. The same phenomenon was also confirmed from Fic et al., for a  $\text{RuO}_2$  electrode in different neutral electrolytes. They observed that the mobility of alkali metal ions rises in the order of  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ . In accordance with the ion shape and dimensions (obtained by modeling) [31], which is shown in **Figure 5**, the high mobility of  $\text{Li}^+$  ions is more favorable for increasing the overall performance of the pseudocapacitive materials.

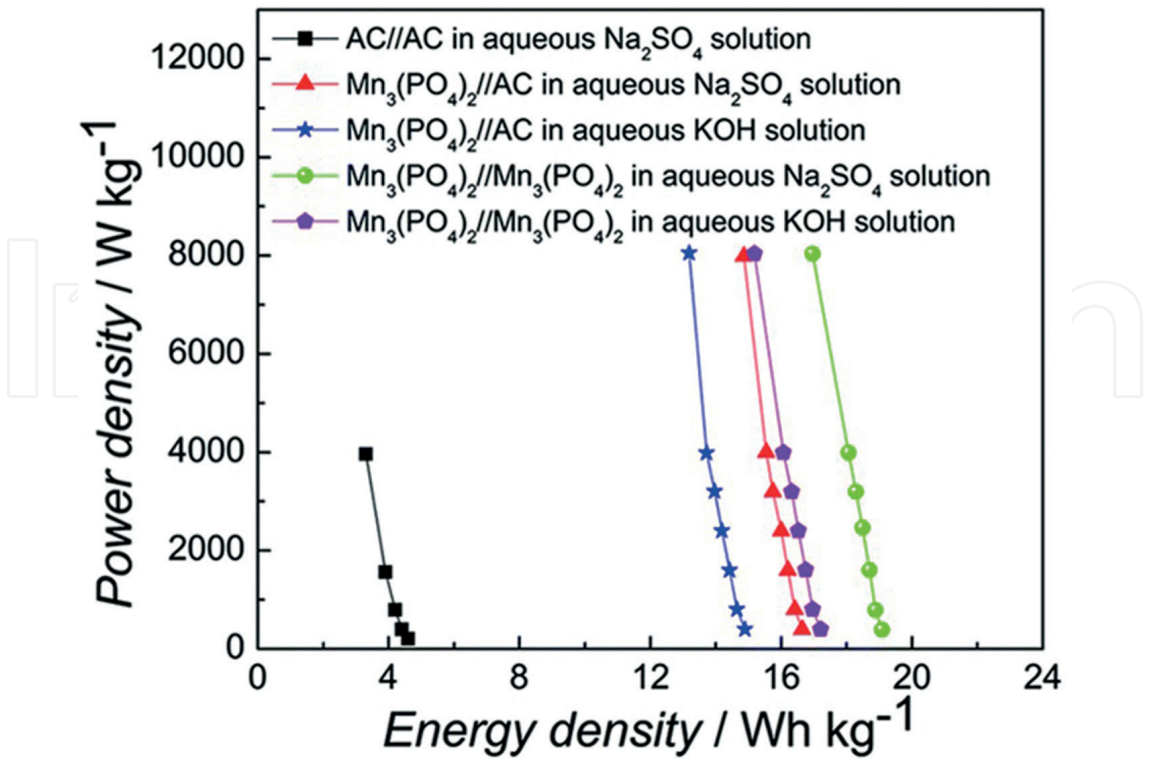
### 3.3.2. Neutral electrolyte-based hybrid supercapacitors

Like EDLC and pseudocapacitive ESs, neutral electrolytes were also utilized for asymmetric supercapacitor devices, which provided a wider range of potential window to achieve high energy density. Though  $\text{MnO}_2$ -based symmetric ESs delivered enough specific capacitance, the operating voltage is limited and so is its overall energy density. The cell working voltage of approximately 1 V was applied for  $\text{MnO}_2$  symmetric devices in many cases. By substituting some carbon materials (CNT and activated carbon) as the negative electrode, the cell voltage of  $\text{MnO}_2$  can be significantly increased [34]. In contrast, manganese phosphate ( $\text{Mn}_3(\text{PO}_4)_2$ )-based symmetric ESs can be performed at an extremely high voltage in the  $\text{Na}_2\text{SO}_4$  electrolyte (~1.8 V); therefore, it reached a maximum energy density of  $19.09 \text{ Wh kg}^{-1}$  [35]. From **Figure 6**, it is noticeable that both symmetric and asymmetric ESs have delivered high energy density in neutral electrolyte rather than the alkaline electrolyte. The reason for this enhanced performance and



**Figure 5.** Ion size and dimensions in aqueous electrolyte obtained by modeling. (Reproduced from [31] with permission from RSC).





**Figure 6.** Ragone plot of  $\text{Mn}_3(\text{PO}_4)_2$ -based symmetric and asymmetric ESs in different neutral electrolytes. (Reproduced from [35] with permission from RSC).

Aqueous electrolyte/ concentration	Electrode material	Cs (F/g)	E (W h kg <sup>-1</sup> )	Potential window (V)	Ref
H <sub>2</sub> SO <sub>4</sub> /0.5 M	RuO <sub>2</sub> -graphene	479	20.28	1.2	[36]
H <sub>2</sub> SO <sub>4</sub> /1 M	Graphene- mesoporous PANI	510	133	1	[37]
H <sub>2</sub> SO <sub>4</sub> /1 M	RuO <sub>2</sub> -carbon nano-onion	570	10.62	1	[21]
KOH/6 M	Graphene	303	6.5	1	[38]
KOH/2 M	NiCo <sub>2</sub> O <sub>4</sub>	1647.6	38	0.41	[39]
KOH/1 M	Ni(OH) <sub>2</sub> /graphene	160	48	1.5	[40]
KOH/6 M	Iron nanosheets/ graphene	720	140	1.2	[41]
KCl/3 M	Ni (OH) <sub>2</sub>	718	–	0.5	[42]
NaOH/1 M	Fe <sub>2</sub> O <sub>3</sub>	178	–	0.5	[43]
Na <sub>2</sub> SO <sub>4</sub> /1 M	CNT/V <sub>2</sub> O <sub>5</sub> nanocomposite// MnO <sub>2</sub> /C	–	16	1.6	[44]
Li <sub>2</sub> SO <sub>4</sub> /1 M	Activated carbon	180	–	2.2	[31]
Na <sub>2</sub> SO <sub>4</sub> /1 M	Hydrous RuO <sub>2</sub>	56.66	18.77	1.6	[45]

**Table 3.** Some important aqueous-based electrolyte supercapacitors and their performance.

high cyclic stability of  $\text{Mn}_3(\text{PO}_4)_2$  is still unclear in neutral electrolyte. To date, several positive and negative electrodes have been investigated for asymmetric supercapacitors in neutral electrolytes, and some of them are given in **Table 3**. The potential window of these asymmetric devices in the series of ~1.5–2.0 V is larger than those described in alkaline and acidic electrolytes.

The advantage of the neutral aqueous electrolytes is not solely solving the corrosion problems of the ESs but also affording a low cost and environmentally friendly choice to enhance the performance of ESs with larger operating voltage and energy density. There are still some challenges to develop the cycle stability of ESs in neutral aqueous electrolytes.

#### 4. Summary and future research directions

In summary, this chapter contributes comprehensive review of the development and modern trends concerning aqueous electrolyte for ESs. The effect of aqueous electrolyte properties including ionic conductivity, ion size, ESPW, etc. on the ES performance like specific capacitance, cyclic stability, energy density, and temperature performance have been reviewed in details. In particular, the effect of interaction among the electrodes and electrolytes has been discussed. This argument shows that the current explored ESs relying on neutral aqueous electrolytes provide numerous benefits such as low cost, environmentally friendly, and safe, over the other electrolyte systems. Despite of considerable accomplishments in this field, still, some difficulties exist such as lower energy density and operating voltage in aqueous electrolytes. To overcome these problems, several research directions can be considered in the future as follows:

1. *Increasing the ESPW values of electrolyte*: In aqueous electrolytes, the ESPW values are dependent on the cations and anions of a given conducting salts. Therefore, the enhancement of the ESPW values could be achieved by finding a new aqueous electrolyte salt and by optimization of the suitable electrolytes.
2. *Enhancing surface area of the pseudocapacitive materials*: As the energy density mainly depends on the capacitance, the performance of ESs could be enhanced by improving charge capacity of the electrode material. Compared to EDLC, the pseudocapacitive material-based symmetric and asymmetric ESs provide higher energy density in aqueous electrolyte. Thus, improving the specific surface area of the pseudocapacitive materials is the promising strategy to enhance the efficiency of ESs.
3. *Building the purity of the aqueous electrolyte*: In some cases, the contamination in electrolyte causes the negative effect on ESPW and also leads to high self-discharge rate. So, it is highly considered to develop the purity of the electrolyte to improve the ES performance.

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