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Toward High-Voltage/Energy Symmetric Supercapacitors via Interface Engineering

Yaqun Wang and Guoxin Zhang

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Abstract

This chapter includes elaborately selected recent literatures on electrochemical energy storing in symmetric supercapacitors (SSCs) with high operating voltages (voltage >1.6 V) and high specific energy. SSCs are a typical sort of electrochemical capacitors with larger energy density than conventional capacitors; by involving electrode materials with stable interfaces (for instance, nitrogen-doped carbon materials) and electrolytes with wide safe potential window (for instance, ionic liquids), they can supply competitive energy relative to batteries. Fundamentals of SSCs are first introduced, aiming at clarifying some critical interfacial phenomena that are critical to enhance overall capacitive performance. State-of-the-art SSCs are included as demonstrations from the aspects of both enhanced capacitances and expanded voltages. We also provide a few feasible strategies for the design high-voltage/energy SSCs such as using inactive electrode materials.

Keywords: symmetric supercapacitor, electrode materials, electrochemical interface, high voltage, high energy

1. Introduction

The growing concerns over fossil fuels, in terms of global warming, pollution, and resource depletion, call for clean and renewable energy such as sunlight, wind, and hydrogen energy [1]. Consequently, great necessity has been urged regarding the development of rapid and efficient energy storage upon the generation of huge amount of the aforementioned types of energy. Supercapacitors (SCs), storing energy in or on the interfaces of electrode materials, are capable of fully charging/discharging within seconds or minutes, making them excellent candidates for the fast accumulation of these transient types of energy [2–4]. Also, taking advantage of the interfacial energy storage mechanism, unlike the deep-conversion mechanism in batteries, SCs

have excellent recyclability, typically >5000 times [5]. The past decade has witnessed significant progresses in SCs researches, many types of SCs have come to existence, including but not limited to electrochemical double-layer capacitors (EDLCs) and asymmetric supercapacitors (ASSCs), and they can be further sorted by applicable electrolytes (mainly three types electrolytes: aqueous, organic, and ionic liquid electrolytes) [2]. Still, they are not satisfactory enough from the perspectives of energy stored, which is mainly due to low capacitances or narrow potential windows especially in aqueous electrolytes [6, 7]. Coupling SCs with pseudo-capacitive electrode materials such as transition metal-based materials or electronically conductive polymers is feasible to enlarge the specific energy; however, the lifetime of pseudo-capacitors normally goes down quickly in a few hundred cycles [8, 9]. Currently, it is still very hard to simultaneously obtain large capacitance, high-operating voltage, and high-cycling stability.

Symmetric supercapacitors (SSCs), mainly including carbon-based EDLCs and a few SSCs with identical metallic component- or conductive polymer-based electrodes, supply much higher specific power and cycling stability than pseudo-capacitors, due to the interfacial charging/discharging mechanism [2, 10]. Their energy are given by the equation (1), in which E is the energy stored in capacitor cell, C_T is the total capacitance, and V is the operating voltage. E is proportional to total capacitance and square voltage, which means that specific energy E can be improved via two ways: increasing specific capacitance and expanding operating voltage [11]. Both of these aforementioned two aspects are highly related to the interfacial chemistry and phenomenon [5]. According to the electrochemical double-layer phenomenon established by Helmholtz, the electrochemical interface consists of electrode surface and thin layered electrolyte (containing ions or cations) adjacent to electrode surface. In the first place, this thin layer of electrolyte plays the fundamental roles of conducting ions and facilitating charge compensation on electrode interface; additionally, they can be decomposed or transformed to supply non-Faradaic current once charge transfer occurs when the electrons arrive in or depart from the conduction band of electrode [6]. Before that, electrolyte ions and molecules are forced to strongly absorb onto electrode surface to form a tightly packed stern layer [6, 7]. According to previous literatures, the efficiency and strength of absorption are highly depend on the surface properties of electrode materials, doping, defect, and functionality and can significantly alter the interactions between electrolyte and electrode interface [11–13]. Therefore, in order to achieve high operating voltage as well as high energy, it is critical to address the interface issues regarding both the surface properties of electrode materials and the applicable electrolytes.

$$E = 1/2 C_T V^2 \quad (1)$$

In the past few decades, many review articles have discussed the investigations on materials selections and device fabrications for developing high-performance SCs, but few accounted for the interface designing and engineering. Also, research progresses from different angles (material synthesis, electrolyte selections, and device fabrications) have come to the point calling for a generic summary for improving the integrated performance of SCs on the clear understanding of electrode interfacial phenomenon. This chapter aims to present and discuss a number of relevant issues, including fundamentals of interfacial (mainly electric double layer (EDL)) capacitance, nanoscale charge transfer, discussions on a few benchmarked

SSCs with large operating voltage and specific energy, and last but not the least, feasibility of safely expanding operating voltage for the achievement of high-energy SSCs. In addition, the importance of carbonaceous electrode materials that are inactive for water splitting is highlighted, in which their specific energy can be significantly improved due to greatly expanded operating voltages. The prospects of SSCs developments are speculated based on the interface engineering on carbonaceous materials, highlighting the practical feasibilities of high-energy SSCs for the progressing smooth swing to renewable energy from traditional fossil fuels.

2. Basics of symmetric supercapacitors (SSCs)

Symmetric supercapacitors (SSCs) are mainly built on electrochemical double-layer configured identical positive and negative electrodes; most applicable electrode materials are carbon-based due to their high chemical stability of carbon materials [1, 14]. The electrochemical double-layer model, first established by Helmholtz, reveals that two oppositely charged ionic layers are formed at electrode-electrolyte interfaces under electrochemical forces driven. Afterward, Stern recognized that there are two regions of ion distribution at the electrode-electrolyte interfaces: one inner layer and one outer layer, as schematically depicted in **Scheme 1**. The inner region, where ions are strongly absorbed onto the electrode surface, is called the compact layer (or Stern layer); and the outer layer consists of a continuous distribution of ions in solution [10]. The capacitance at electrode-electrolyte interface (C_{EDL}) with electrochemical double-layer configuration can be divided into capacitance from the inner compact layer (C_H) and capacitance from the diffuse layer (C_{Diff}), as described in equation (2)

$$\frac{1}{C_{EDL}} = \frac{1}{C_H} + \frac{1}{C_{Diff}} \quad (2)$$

There are several critical factors that give significant impact on C_{EDL} , mainly including the conductivity of electrode material, the surface area of electrode materials, the accessibility to the inner electrochemical surface, the electric field across the electrode, and the electrolyte/solvent properties [15]. For instance, SCs with high-surface area porous carbon electrode materials (such as activated carbon) can store much more capacitances by several orders of magnitude. There are also a few other ways that are feasible to enlarge the capacitances including doping heteroatom elements and compositing stable metal oxides or conductive polymers [11, 16]. Heteroatom doping is able to break down the high symmetry of graphitic carbon, creating a large amount of defects, leading to the easy formation of compact inner absorption layer [16]. The advantages of using stable metal oxides or conductive polymers as electrochemical interfaces instead of carbon materials are obvious; they are capable of supplying much more capacitance through pseudo-capacitive absorption besides the EDL capacitance [17]. However, the greatly enlarged capacitances are often obtained on the basis of compromising the efficiency and cycling stability, and only a minor few metal oxides and conductive polymers are qualified due to conductivity and cost issues, which we will summarize later in Section 3.

Besides the electrode materials selection, it is also important to choose a proper electrolyte and solvent to form a robust electrode-electrolyte interface since energy stored in a SSCs

Scheme 1. Schematic representations of the cross-sectional EDL structure of electrode/electrolyte interface.

device is governed by the square of operating voltage multiplying capacitance, as described in equation (1). Relative to capacitance, operating voltage actually gives bigger impact on the specific energy of the whole SSCs device. Therefore, pushing the operating voltage to the limit by means of choosing proper electrolyte solution is of significant practical meanings, a robust electrode-electrolyte interface can efficiently prevent the nanoscale charge transfer at the interfaces, thus to largely expand the applicable operating voltage and to enhance the specific energy [6]. In general, electrode-electrolyte interfaces formed in ionic liquid are more stable than in organic solvents, and then in aqueous solution, which is governed by the chemical stable window of solvents [6]. Typically, the chemical stability of the abovementioned three types of electrolytes follows the sequence of ionic liquid > organic electrolyte > aqueous electrolyte. For instance, an ionic liquid electrolyte can deliver a potential window as wide as 4.0 V, while aqueous electrolyte can only supply a 1.23-V wide potential window due to water splitting at 1.23 V [18, 19]. However, in some aqueous cases, by suppressing the activity of water splitting such as in neutral electrolytes, the safe operating voltage can be largely expanded to 1.8 V [20, 21]. The operating voltage can be further enlarged by applying electrode material that has much less activity toward water splitting, leading to a 2.0-V safe operating voltage, which is clearly achieved by mediating the interface properties [22]. The discussion on interface engineering for safe voltage expansion is placed in Section 4.

3. High-capacitance electrode materials for SSCs

Symmetric supercapacitors (SSCs), as one typical sort of SCs, though are able to provide charging/discharging in several minutes, deliver incomparable capacitance as to secondary batteries (such as Li-ion battery) [23]. Therefore, it is crucial to enlarge the specific energy stored in each electrode by either optimizing existed electrode materials or developing new types of materials. For now, carbon-based materials contribute to most of electrode materials

used in SSCs due to their abundant sources, low costs, high porosity, excellent chemical stability, and conductivity [1, 13]. Considering the mechanism of energy stored in a SSC to be mainly dominated by electrical double-layer configurations, the overall performance of full SSCs is restricted below this value. Therefore, exploring high-performance electrode materials is urgent in order to achieve high-energy SSCs. There are mainly two types of commonly used materials: carbon-based materials and pseudo-capacitive materials, which we will separately describe in the following paragraphs.

3.1. Carbon-based materials

As mentioned in Section 2, EDL-configured SCs are mainly based on various kinds of carbon materials such as activated carbon (AC). In this specific part, the general ways of enlarging capacitance of carbon-based materials are first summarized via giving representative example. Generally speaking, three ways can be utilized to achieve these goals: (1) increasing the electrochemically accessible surface area (EASA), (2) creating more anchoring sites for charge carriers, and (3) involving few amounts of pseudo-capacitance on the basis of EDL capacitance [4, 15, 24]. As followed, we will give explanations on the latter two strategies; the foremost strategy of enlarging EASA is only for listing because it involves a very few interfacial chemistries, which is not our main topic here in this chapter.

The charming feature of carbon materials is mostly founded on the largely conjugated aromatic six-atom ringed carbon that create huge amount of delocalized electrons, for instance, graphene, one typical allotrope of carbon, have an ultrahigh charge carrier mobility of $200,000 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ [25]. Meanwhile, the large conjugation system of graphitized carbon intrinsically generates highly symmetric molecular structure. The superlarge conjugation system, on one hand, enables fast transportation of charge carriers and, on the other hand, leaves very few sites for ions to absorb. From this specific aspect, doping heteroatom species and creating defects in graphitic carbon lattice can significantly boost the apparent capacitance by providing more sites for ions anchoring, as depicted in **Scheme 2** [26]. In some cases, very strong chemical binding on heavily doped carbon sites can even generate charge transfer to achieve much larger capacitance [16, 27]. Therefore, if let a small proportion of conductivity sacrificed, desirably larger capacitances can be obtained via simply involving more heteroatom sites especially containing nitrogen species [11].

Activated carbons (AC) are the most commonly used electrode materials in SSCs because of their large surface areas and low costs. ACs are usually converted from carbon-rich chemicals and biomasses under the high-temperature activation of chemicals such as KOH, ZnCl_2 , and H_3PO_4 [28, 29]. Although, very high porosity is obtained, most of the heteroatom-containing functionalities and moieties are forced to be removed by the disturbance of high temperature [30]. The as-formed clean carbon surface may probably leave very limited sites that are readily to absorb ions, so the most obtainable capacitance using AC electrode materials are falling in $100\text{--}200 \text{ F g}^{-1}$. Thanks to the abundant chemistry of carbon species, most of inorganic elements can connect with carbon to break the symmetry of $\pi\text{--}\pi$ conjugation and also to include partial pseudo-capacitive sites for higher capacitance [11]. For instance, a nitrogen-doped porous carbon (N content $\sim 12 \text{ at.}\%$) reported by Huang et al. delivered an ultrahigh capacitance of 855 F g^{-1} and a high specific energy of 41 Wh kg^{-1} in aqueous electrolytes. The improvement

Scheme 2. Aromatic carbon lattices can embrace many types of heteroatom doping such as nitrogen (blue), oxygen (green), sulfur (pink), and so on. Defective carbon sites (red) that are unsaturated can also be treated as anchoring sites for ions.

mostly originates from robust redox reactions at electrochemically active nitrogen-containing sites that transform inert graphene-like layered carbon [16]. A nitrogen, sulfur-co-doped carbon fabricated by Sun et al. exhibited a very high specific capacitance of 427 F g^{-1} at 1.0 A g^{-1} and still showed an excellent capacitance of 270 F g^{-1} at superhigh current density of 100 A g^{-1} (**Figure 1**) [31]. However, the dopant content shall be controlled under an optimistic level; otherwise, the capacitance will not be increased because of severely damaged conductivity. For instance, Cheng et al. fabricated a high level of N, S, or B doping graphene, also called superdoping, achieving 29.82, 17.55, and 10.79 at% for N-, S-, and B-doping, respectively [32]. However, the 29.82 at%-N-doped graphene achieved a medium specific capacitance of 354 F g^{-1} while the pristine graphene without any doping obtained a specific capacitance of 213 F g^{-1} (taking 60% of heavily N-doped graphene).

Figure 1. (a) SEM image and (b) XPS survey of NS-co-doped carbon materials. (c) Gravimetric capacitance of NS-co-doped carbon materials made SSCs in three aqueous electrolytes. Adapted with permission [31]. Copyright 2017, American Chemical Society.

3.2. Interfacial pseudo-capacitive materials

Pseudo-capacitance is achieved by Faradaic electron charge-transfer with redox reactions, intercalation or electro-sorption. Unlike electrochemical double-layer supercapacitor, pseudo-supercapacitor use electronically conducting polymers (ECPs) or stable metal oxides electrodes can achieve balanced capacitive performance of much enhanced capacitance and fairly good rate/cycling performance.

3.2.1. Electronically conducting polymers (ECPs)

ECPs are one typical sort of pseudo-capacitive materials that can engage electrochemical doping or redox reaction with anions and cations, many ECPs such as polyaniline (PANI), polypyrrole (PPy), and derivatives of polythiophene (PTh) have been widely applied in supercapacitors due to their large capacitances, flexibility, and low costs. The typical dopant level for these polymers as well as typical specific capacitances and applicable voltage ranges are given in **Table 1**. The mechanism of ECPs storing charges can be described by the following two formulas, *i.e.*, *p*-doping upon oxidization and *n*-doping upon reduction.

ECPs-made SSCs can be sorted into two categories: Type I-using the same *p*-doped ECPs for both electrodes and Type II-using the same ECPs but using different forms of ECPs as electrodes (*p*-doped form as positive electrode and *n*-doped form as negative electrode). When the Type I SSCs is charged, the positive electrode is completely oxidized while the negative electrode remains neutral, which supplies 0.5–0.75 V potential difference. When it is discharged, both electrodes are semi-oxidized, which makes only 50% of the *p*-doped capacitance can be used. In addition, the supplied potential of Type II SSCs is higher compared with Type I SSCs. This improvement would result in high specific energy due to much larger difference of square voltage (V^2).

Conducting polymer	Mw (g mol ⁻¹)	Conductivity (S cm ⁻¹)	Dopant level	Potential range (V)	Theoretical specific capacitance (F g ⁻¹)
PANI	93	0.01–5	0.5	0.7	750
PPy	67	0.3–100	0.33	0.8	620
PTh	84	2–150	0.33	0.8	485
PEDOT	142	300–500	0.33	1.2	210

Mw is molecular weight per unit monomer (g mol⁻¹) PANI is polyaniline, PPy is polypyrrole, PTh is polythiophene and PEDOT is poly (3,4-ethylenedioxythiophene).

Table 1. Theoretical specific capacitance of conducting polymers.

Many ECPs such as PANI and PPy can only be *p*-doped due to the very negative potentials required for *n*-doping, if compared with the reduction potential limit of molecular solvent-based electrolytes. For instance, Pan et al. synthesized PANI hydrogel with high surface area and three-dimensional porous nanostructures and demonstrated that the as-obtained PANI-based supercapacitor could supply a very large specific capacitance of 480 F g^{-1} , excellent rate capability, and very good cycling stability of 83% capacitance retention after 10,000 cycles but only provide a safe operating voltage of 0.8 V for SSCs. Unique three-dimensional (3D) microstructure by interconnected polymer (**Figure 2**) by Yu et al. exhibit good mechanical properties and high rate performance with specific capacitance of 400 F g^{-1} , excellent rate capability [33]. On the contrary, PTh and its derivatives can be used as *n*-doped ECPs; however, the conductivity of these ECPs after *n*-doping is not very high in the reduced state and thus leads to a low capacitance in the negative potential region [34]. For example, Stenger-smith et al. developed poly (3,4-propylenedioxythiophene) and poly(3,4-ethylenedioxythiophene) as electrode couples show good cycle life [35].

3.2.2. Transition metal oxides

Transition metal oxides show high pseudo-capacitive behavior with redox chemistry both on and in the interfaces, which have been extensively studied due to high specific capacitance. There are several commonly studied stable metal oxide materials such as RuO_2 (theoretical specific capacitance $\sim 1000 \text{ F g}^{-1}$) and MnO_2 (theoretical specific capacitance: $1100\text{--}1300 \text{ F g}^{-1}$) [36]. RuO_2 is one of the most explored electrode materials due to the high specific pseudo-capacitance,

Figure 2. (a) Illustration depicting controlled synthesis of the CuPcTs doped PPy hydrogel. (b) SEM images of nanostructured PPy hydrogel. (c) Specific capacitance as a function of current density for CuPcTs-PPy and pristine PPy. Adapted with permission [31]. Copyright 2017, American Chemical Society.

reversible redox reaction, and long cycling life. For instance, RuO_2 can supply a safe operating voltage of 0.7 V in SSCs [37]. Due to the very high costs, RuO_2 is often limited in aerospace and military application. While MnO_2 is generally studied because of their low cost, low toxicity, environmental friendliness, and high theoretical capacitances (up to $1100\text{--}1300 \text{ F g}^{-1}$) [38–40]. The main mechanism of the pseudo-capacitive energy storage in MnO_2 is attributed to a reversible intercalation/de-intercalation of protons or an adsorption of cations such as Li^+ , Na^+ , K^+ from electrolytes [39, 41]. These can be expressed by the following formula:

where X^+ represents the protons and alkali metal cations (Li^+ , Na^+ , K^+) in the electrolyte. Toupin and coworkers believed that the pseudo-capacitances are mainly occurring in the interfaces due to the difficulty of the protons or cations transportation into the bulk phase materials [38, 42–44].

3.2.3. Composites materials

Usually, the specific capacitance can be improved by tuning morphology, surface area, and porous structure of active material. The most common electrode materials are carbon materials, metal oxides, and ECPs. To maximize the advantages of these materials, composite materials are of great technological advantages due to the combination of the intrinsic properties of each component as well as the synergistic effect resulting from the hybrids. The composites of carbon materials with other materials such as ECPs and metal oxides, which often use carbon materials as substrate, for example, carbon nanotubes, carbon fibers, graphene materials, activated carbon, etc. As depicted in Section 3.2, ECPs and metal oxides are highly promising active electrode materials but these materials suffer from severe cycling stability problems because of the structure collapse caused by swelling and shrinking during charging/discharging. Hybridizing carbon materials with ECPs and/or metal oxides can synergistically boost nearly all the aspects of capacitive performance including conductivity, capacitance, and cycling stability. For instance, Peng et al. fabricated hollow fiber electrodes using reduced graphene oxide (RGO)/ECPs, simultaneously achieving large areal capacitance (304.5 mF cm^{-2}), high flexibility, and high electrical conductivity [45].

4. Electrolyte-mediated operating voltage

Electrolyte is one of the key components of SCs, basically, conveying ionic current and leading the formation of electrical double layer, more importantly, under certain circumstances of matched electrode materials and electrolytes, and facilitating reversible redox processes for larger amount of charges stored in the interfaces. In general, electrolytes used in SSCs can be sorted into two main categories: liquid electrolytes and solid/quasi-solid state electrolytes. Liquid electrolytes can be further sorted into three groups: aqueous electrolytes, organic electrolytes, and ionic liquids (ILs), while solid/quasi-solid state electrolytes can be divided into organic electrolytes and inorganic electrolytes [7]. There is no once-for-all solution for electrolyte selection, each electrolyte has its own advantages and disadvantages. For

instance, in the group of liquid electrolytes, aqueous electrolytes exhibit very high ionic conductivity, low costs, and high safety, yet they can only deliver an operating potential window of about 1.0–1.3 V because the water splitting potential window is about 1.23 V. While the organic electrolytes and IL electrolytes can be operated at much higher voltages, typically organic electrolytes at 2.5–2.7 and IL electrolytes at 3.5–4.0 V. However, the expensive costs and potential risks for environment strongly hinder their practical applications. According to previous literatures, many aspects of electrolytes can have significant influence on the capacitive performance; here, in this short chapter, we focus on two main aspects: (a) the interaction between electrolyte and electrode materials and (b) the stable potential window. We will discuss the abovementioned two important aspects according to different types of liquid electrolytes (Table 2).

4.1. Aqueous electrolytes

There are many advantageous merits of aqueous electrolytes, for instance, high ionic conductivity (up to ~1 S cm⁻¹) that can deliver very high power density, high safety that greatly simplifies the fabrication and assembly processes, and low costs that enables broad practical applications. Generally, aqueous electrolytes have three main classes: acidic electrolytes (H₂SO₄, H₃PO₄, etc.), basic electrolytes (KOH, NaOH, etc.), and neutral electrolytes (Li₂SO₄, Na₂SO₄, NaCl, etc.). Due to the narrow chemically stable window of water, the operable voltages for SSCs assembled using aqueous electrolytes are usually lying within 1 V. Consequently, the energy stored in single one SSCs is limited, which is far less competitive with organic and IL SSCs, not to mention batteries. Many efforts have been taken to broaden the safe working voltage of aqueous SSCs, which is mainly through the suppression of water splitting at electrode interfaces.

To understand the phenomenon occurring at the electrode/electrolyte interfaces, we need to look into the details of potential-driven water splitting at electrode interfaces. Water splitting basically requires three main steps: absorption, conversion, and desorption. Take water

	Aqueous electrolyte	Organic electrolyte	Ionic liquid
Operation voltage window (V)	≤1.2	2.5–2.8	2–6
Ionic conductivity, σ (ms cm ⁻¹)	High	Low	Very low
Viscosity, η	Low	Medium/high	High
Cost	Low	Medium/high	Very high
Work temperature	Narrow	Wide	Wide
Toxicity	Low	Medium/high	Low
Advantage	High conductivity	High voltage window	High thermal and chemical stability, wide voltage window
Disadvantage	Low voltage window	Large electrolyte ions, low conductivity,	High viscosity

Table 2. The comparative properties of different types of electrolytes.

oxidation as example, H_2O molecules and OH^- can both act as feeds for water oxidation while OH^- serve as charge carriers to provide capacitance. Initially, these oxygen-containing species are strongly absorbed on electrode surface to supply EDL capacitance. Once the binding force driven by applied potential was large enough the dielectric layer becomes conductive for electron, the excessive electron in OH^- would be readily transferred from OH^- to current collector. After complex processes of H^+ depletion, $\text{O}=\text{O}$ bond formation, and desorption of O_2 , the water splitting at cathode is completed, as schematically depicted in **Scheme 3**. There seems to be one threshold for the absorption mode turning from capacitive absorption to water splitting, and this threshold is highly related with the toughness of absorption and the capability of electrode materials catalyzing the complex processes for water splitting and also the potential applied.

In order to broaden the operating voltage window of SSCs, it is feasible through the suppression of splitting of electrolytes, for instance, in aqueous electrolytes, that can be done through the passivation of water splitting activity on the water splitting-inactive electrode surface. For instance, Zheng et al. developed a conductive polymer of poly(naphthalene four formyl ethylenediamine) (PNTE) and used them as anode materials for aqueous rechargeable Li-ion battery. The passivated hydrogen evolution activity of PNFE exhibited very large overpotential for HER and thus enabled a capacitor-like Li^+ storage kinetics in aqueous electrolytes [46]. Thereafter, Zhang et al. reported the fabrication of highly porous carbon materials with high carbon content (>93 at.%) and limited heteroatom doping. The as-synthesized carbon materials exhibited very sluggish water splitting performance, their stably operated voltage window for water splitting can be greatly broadened to 2.2 V or even higher on the carbon materials in neutral Li_2SO_4 electrolyte, as shown in **Figure 3** [47]. Normally, water molecules can be split into hydrogen and oxygen at 1.3–1.8 V, depending on the types of aqueous electrolytes applied.

Scheme 3. Schematic depictions of (a) capacitive absorption and (b) water oxidation.

Figure 3. Hydrogen evolution and oxygen evolution reaction performance of non-doped porous carbon materials (NDPC-6/7/8) measured in (a) 0.5 M H₂SO₄ and (b) 0.1 M KOH, respectively. (c) CV profiles of NDPC-8 with different applied voltage windows, (d) GCD profiles of NDPC-8 with different current densities. Adapted with permission [47]. Copyright 2017, Royal Society of Chemistry.

Therefore, on the basis of large surface area, conductive electrode network, and proper electrolyte, the enlargement of operation voltage can be further realized through the application of electrode materials that have sluggish activity toward splitting of electrolytes. For example, it is feasible to use highly porous high-carbon content materials as electrode materials and Li₂SO₄ solution as electrolyte for the assembly of SSCs with wide operating voltage window.

4.2. Organic electrolytes

The specific energy of aqueous SSCs was mainly limited by the water splitting voltage at ~1.23 V. Therefore, organic electrolytes with high conductivity, wide electrochemical voltage window, excellent chemical stability and acceptable cost become the mainstream electrolytes in practical supercapacitor market. Organic electrolytes consist of organic solvents and salts, usually have an operating voltage up to 2.7 V or higher, which makes it highly attractive for high-energy SSCs [48]. Since the organic electrolytes contain two parts, we will give separate illustrations.

First, proper organic solvents can be chosen based on the following rules: high solubility for electrolyte salts, low viscosity to facilitate ionic transport, no side reaction with other parts of supercapacitor (including active materials, current collector, and separator), wide work temperature, and environmental friendliness. Among all organic electrolytes, the most widely used solvents are acetonitrile (AN) and propylene carbonate (PC). AN is capable of dissolving large quantities of salts but it is toxic and risky to environment. PC, a green solvent, has been widely used, meanwhile, it also has very wide stable working temperature and good conductivity. Also, other electrolytes such as γ -butyrolactone (GBL), N,N-dimethylformamide (DMF), N-methylpyrrolidone (NMP), N,N-dimethylacetamide (DMA) are applicable electrolytes that have been widely studied.

Second, the most common used electrolyte salts are chain-like quaternary ammonium salts such as tetraethylammonium tetrafluoroborate (TEA-BF₄) and triethylmethylammonium tetrafluoroborate (TEMA-BF₄) [49]. One feasible method to further enlarge the operating voltage window for organic electrolyte is through the increasing of electrolyte salts concentration. On one hand, one can find the optimized salt concentration that has the best solubility and chemical stability; on the other hand, it is one feasible way to thicken the layer of charge carriers instead of solvent molecule layer at the electrode/electrolyte interfaces. For instance, 1 mol L⁻¹ spiro-bipyrrolidinium tetrafluoroborate (SBP-BF₄) in PC solvent showed very high electrochemical stability on the interface due to its spiro rings molecular structure [50]. Yu et al. reported 1.5 mol L⁻¹ SBP-BF₄/PC shows higher conductivity of 17 mS cm⁻¹ than 1.5 mol L⁻¹ TEMA-BF₄/PC [51]. Other metal salt such as lithium/sodium salt are also applicable in carbon-based SSCs following the same rules for electrolyte picking up.

4.3. Ionic liquid electrolytes

Low-temperature ionic liquids (ILs) are pure organic salts containing no solvents with melting points below 100°C. If the liquid state can maintain at ambient temperature, they are called room temperature ionic liquids (RTILs). RTIL are the type of ILs of broad interests to supercapacitors especially SSCs due to their unique properties including non-volatility, poor combustibility and high resistance to heat. However, the ionic conductivity of ILs usually fall in 0.1–15 mS cm⁻¹, which is much lower than most of the commercial organic electrolytes. But ILs can show excellent conductivity at high temperature because of low viscosity. Many kinds of ILs have been widely used in supercapacitor; the two pairing ions of imidazole and pyrrole are most commonly studied. Generally speaking, the size and symmetry of cations strongly influence the melting points of ionic liquids. Normally, the imidazole possesses high conductivity with narrow potential window, alkylpyrrole shows wide operating voltage but high melting point. For instance, Chen et al. used a series of sponge-like carbon as electrode and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) and 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆) as electrolytes; the gravimetric capacitance of as-made SSCs can be improved to 445 F g⁻¹ with a high discharge voltage of 4 V, very good rate capability, and cycling stability [52].

5. Conclusions and perspectives

There have been many strategies proposed to pursue high-energy symmetric supercapacitors (SSCs), including two main parts: (1) the electrode materials' selection and design and (2) the electrolyte optimization. As described in Section 3, commonly, desirable electrode materials (mainly carbon-based materials) for SSCs can be obtained by meeting the following criterions: large specific surface area, hierarchical porosity, optimized heteroatom doping, and compositing with pseudo-capacitive materials such as electronically conductive polymers (ECPs) or stable metal oxides. Section 4 summarized the commonly used electrolytes and illustrated a few key principles of how to select a proper electrolyte for SSCs for different purposes. Three main types of liquid electrolytes: aqueous electrolytes, organic electrolytes, and ionic liquids (ILs) electrolytes hold different advantages, for instance, aqueous ones are low cost and highly ionic conductive while organic and IL ones can be operated at high voltages. However, there are also limits for each type of electrolytes, for example, the operating voltages of aqueous electrolytes are restricted in between 1.0 and 1.8 V and organic and ILs electrolytes are expensive and risky to environments. Based on the abovementioned advances in supercapacitors, we provided two feasible ways to further improve the capacitive performance of SSCs about the interface-related subjects, including (1) optimizing the types and contents of heteroatom dopants to involve pseudo-capacitance and expand the operating voltage by suppressing the activity of splitting electrolytes and (2) designing new types of electrolytes such as aqueous electrolytes containing neutral salts (Li_2SO_4 , Li-TFSI, etc.). In conclusion, on the basis of proper electrode/electrolyte's selection, we can achieve further development in SSCs through engineering the abovementioned two important aspects that are used for the construction of robust electrode/electrolyte interface.

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Conflict of interest

All authors declare that they have no conflict of interests.

Appendices and Nomenclature

SSCs	symmetric supercapacitors
SCs	supercapacitors

EDLCs	electrochemical double-layer capacitors
ASSCs	asymmetric supercapacitors
AC	activated carbon
EASA	electrochemically accessible surface area
ECPs	electronically conducting polymers
PANI	polyaniline
PPy	polypyrrole
PTh	polythiophene
ILs	ionic liquids
PNTE	polynaphthalene four formyl ethylenediamine
NDPC	non-doped porous carbon materials
AN	acetonitrile
PC	propylene carbonate
GBL	γ -butyrolactone
DMF	N,N-dimethylformamide
NMP	N-methylpyrrolidone
DMA	N,N-dimethylacetamide
TEMA-BF ₄	triethylmethylammonium tetrafluoroborate
SBP-BF ₄	spiro-bipyrrolidinium tetrafluoroborate
EMIM-BF ₄	tetrafluoroborate

Author details

Yaqun Wang and Guoxin Zhang*

*Address all correspondence to: zhanggx@sdust.edu.cn

College of Electrical Engineering and Automation, Shandong University of Science and Technology, Tsingtao, China

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