A REVIEW OF METAL OXIDE COMPOSITE ELECTRODE MATERIALS FOR ELECTROCHEMICAL CAPACITORS

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With the emerging technology in the 21st century, which requires higher electrochemical performances, metal oxide composite electrodes in particular offer complementary properties of individual materials via the incorporation of both physical and chemical charge storage mechanism together in a single electrode. Numerous works reviewed herein have identified a wide variety of attractive metal oxide-based composite electrode material for symmetric and asymmetric electrochemical capacitors. The focus of the review is the detailed literature data and discussion regarding the electrochemical performance of various metal oxide composite electrodes fabricated from different configurations including binary and ternary composites. Additionally, projection of future development in hybrid capacitor coupling lithium metal oxides and carbonaceous materials are found to obtain significantly higher energy storage than currently available commercial electrochemical capacitors. This review describes the novel concept of lithium metal oxide electrode materials which are of value to researchers in developing high-energy and
enhanced-cyclability electrochemical capacitors comparable to Li-ion batteries. In order to fully exploit the potential of metal oxide composite electrode materials, developing low cost, environment-friendly nanocomposite electrodes is certainly a research direction that should be extensively investigated in the future.

**Keywords:** Electrochemical capacitors; composite electrode; metal oxides; lithium metal oxides.

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### 1. Introduction

Demand for energy consumption has significantly increased due to the rapid growth of population and global economy. Based on the surveys on total world energy consumption conducted by Energy Information Administration (EIA), fossil fuels (petroleum, coal, natural gas, etc.) make up the bulk of the world’s current primary energy sources.\(^1\) Excessive dependence on fossil fuels has resulted in increasing greenhouse gas emission, rising oil prices and fossil fuel depletion which consequently lead to global economic crisis and environmental issues. Therefore, transforming natural energy from sustainable and renewable resources such as the sun, ocean tides and wind could help meet increased energy needs. However, man has limited control over natural phenomena due to the climate/geographical constraints. For these reasons, energy storage technology appears as one of the most promising options in harvesting renewably-generated electrical energy during the optimum production period for future use.

Of the available electrical energy storage devices, fuel cells, batteries and capacitors have been the technology of choice for most applications. Each of these system exhibits different characteristics in terms of specific energy and power, as shown in the Ragone plot (Fig. 1). In general, batteries can store the highest specific energy ranges from 120 Wh/kg to 200 Wh/kg with relatively low specific power, ranging from 0.4 kW/kg to 3 kW/kg.\(^2\) On the other hand, conventional capacitors deliver relatively very low specific energy (< 0.1 Wh/kg). Comparatively, the electrochemical capacitors have much higher specific power (from 5 kW/kg to 55 kW/kg) and reasonable specific energy (4 Wh/kg to 8 Wh/kg), which are likely to bridge the function for the energy/power gap between the conventional capacitors and batteries.\(^2\)

Electrochemical capacitors, also well known as supercapacitors, have evolved through several generations of designs since commercial introduction of NEC’s Supercapacitor in 1978.\(^8\) The conventional electrochemical capacitor design technology, which is better known as electric double layer capacitor (EDLC), employs two identical polarizable electrodes (carbon electrodes) in aqueous electrolyte that typically rely on the adsorption of ions from electrolyte onto the high surface area of the electrodes.\(^4\) Second-generation symmetric devices were introduced in the 1980s, which used a nonaqueous electrolyte (organic electrolyte) to increase the cell operating voltage. The symmetric technology is also applied to the arrangement where both composite electrodes are made of metal oxides/conducting polymers and carbon materials.\(^4\) Third-generation electrochemical capacitors incorporate both polarizable electrode (carbon) and a nonpolarizable electrode (metal oxide or conducting polymer) within a same electrochemical system.\(^5\) This design is referred to as hybrid capacitor. This new technology demonstrates superior performance compared to the conventional electrochemical capacitors: improved safety, higher specific energy, more stable operating voltage, lower materials/manufacturing costs and...
voltage self-balancing in high-voltage strings of capacitor cells.\textsuperscript{5}

The principle of charge separation and charge storage characteristics was discovered by both Dutch physicist Pieter van Musschenbroek and German experimenter Ewald G. von Kleist when they invented and developed a Leyden jar independently in the middle of 1800s.\textsuperscript{6} It was the first device capable of storing electric charge, which consisted of glass jar with conducting metal foil coating on inner and outer surfaces. The inner and outer surfaces of the jar are separated by the insulating glass and able to store equal but opposite charges when an electric generator is connected to the inner surface while the outer is grounded. Subsequently, the concept of electric double-layer capacitance was described by Helmholtz in 1853 as a simple capacitor based on a physical model in which a single layer of ions was adsorbed at the surface.\textsuperscript{7} Nevertheless, the Helmholtz model does not predict the variation of experimental capacitance values. The Helmholtz model was later refined by Gouy and Chapman by introducing a diffuse model of the electric double layer, from which the electric potential decreases exponentially away from the surface to the fluid bulk in the early 1900's.\textsuperscript{8} However, the assumption made in the Gouy–Chapman model has its limitation in the calculation of the double-layer capacitance which only approached true values near the point of zero charge (PZC).\textsuperscript{8} Consequently, Stern proposed the combination of the Helmholtz and the Gouy–Chapman models, thereafter named the Stern model in 1924, incorporating the compact layers and the diffuse layer and giving much improved prediction of electrode capacitance.\textsuperscript{9} However, this model offers no explanation why counterions in electrolyte do not move over to electrode surface. In 1963, Bockris and co-workers developed the Stern model and suggested a model that includes the action of adsorbed water dipoles within the inner Helmholtz plane (IHP). The effect of hydration sheath around cations in double layer system explains the sound reason why anions could not move closer to the electrode but only approach the outer Helmholtz plane (OHP).\textsuperscript{10} The model is theoretically plausible and is currently widely accepted.\textsuperscript{10}

The earliest patent was filed in 1957 by General Electric for an electrochemical capacitor using porous carbon electrodes.\textsuperscript{11} Later in 1966, Standard Oil Company of Ohio (SOHIO) patented a device that stored energy in a double layer at the interface between carbon electrodes and aqueous electrolyte, achieved by ionic adsorption.\textsuperscript{12} Four years later, SOHIO patented another disc-shaped capacitor incorporating a carbon paste electrode with a separator soaked in an electrolyte.\textsuperscript{13} The first commercial double-layer capacitor was introduced in 1978.\textsuperscript{12} However, not until the electric and hybrid vehicle program initiated by the United State Department of Energy (DoE) in 1989, did electrochemical capacitor embark its milestone in energy storage technology.\textsuperscript{11} Further increased demands for green energy and higher power quantity, have led to the recognition that electrochemical capacitors could be complementary to batteries or fuel cells in energy storage applications.\textsuperscript{11} Many other governments have also engaged actively in exploring, researching and developing electrochemical capacitor technologies. Considerable companies continue investing time and money in the research and development of Electrochemical capacitor, namely, Cooper, Evans, AVX, Maxwell and IOXUS in the United States, Tavrima in Canada, Cornell Dubilier in UK, Saft in France, WIMA in Germany, Cellergy in Israel, NEC and Panasonice in Japan, Cap-XX in Australia, Nesscap and Vinatech in Korea, and ESMA in Russia.\textsuperscript{11} Current markets address a large majority of their electrochemical capacitors using symmetric activated carbon (AC) electrode materials with acetonitrile-based organic electrolyte.\textsuperscript{8}

As a result of low cost, easy availability, large active area and good electric conductivity, carbon-based materials currently dominate the market as core electrode materials.\textsuperscript{14} However, the exploitation of pseudocapactive effects to enhance double-layer capacitance seems to be an alternative means to develop the next generation of high-power and high-energy electrochemical capacitors. However, pseudocapacitors frequently suffer a number of undesirable shortcomings including charge storage instability, an increased resistance, short life cycle and higher manufacturing cost compared to those of carbon-based electrodes.\textsuperscript{15} Recent developments of composite materials which integrate carbon-based materials with either metal oxide or conducting polymer have demonstrated the improved capacitive performance and cycle life through the synergistic effect of both EDLC and pseudocapacitance mechanisms. Carbon-based materials provide a high-surface area backbone that increases the
contact between the deposited active materials and electrolyte while pseudocapacitive materials enhance the capacitance of composite electrode through Faradaic reactions. Similar to this concept, hybrid capacitor utilizing battery-type and capacitor-type electrodes are reported to obtain significantly higher energy storage than the currently available commercial electrochemical capacitors.\textsuperscript{16} The exciting growth of advanced nanostructured materials has driven the impressive development in the research of metal oxide composite electrodes. Numerous combinations of positive and negative electrodes have been extensively studied in aqueous or organic electrolytes. Although metal oxide composite electrodes generally exhibit much improved capacitive performance and significantly enhanced energy density in comparison to conventional electrochemical capacitors, the limited cycle stability of the Faradaic electrodes remain as challenge to these hybrid capacitors. Cost and environmental friendliness of materials also remains the keys to explore novel composite electrode materials.

2. Principles of Electrochemical Capacitor

Electrochemical capacitors differ from conventional capacitors by storing charge using the double-layer concept in the absence of insulating dielectric material.\textsuperscript{17} The positive and negative ionic charges from electrolyte accumulate at the surface of conductive electrodes, compensating the opposite electronic charges at electrode surfaces.\textsuperscript{18} As a result, double-layer capacitance arises at the interface between electrodes and electrolyte, according to Eq. (1):

\[
C_{dl} = \frac{\varepsilon_0 \varepsilon_r}{d} A,
\]

where \(\varepsilon_0\) is the space permittivity and \(\varepsilon_r\) is the relative permittivity, \(A\) is the surface area of an electrode and \(d\) is the effective thickness of the double layer. The term \(d\) which represents the separation distance between the electrodes in the conventional capacitor, is now referring to the effective thickness of the double layer at the solid/electrolyte interface. The separation of the charges at the interface typically is only in the order of few angstroms, depending on the electrolytes used.\textsuperscript{19} As a result of high internal surface area of the electrodes and nanometer scale thickness of the double layer, the capacitances obtained in electrochemical capacitors are several orders of magnitude higher than those of conventional capacitors of the same size.\textsuperscript{6} In terms of design and manufacturing, electrochemical capacitors are similar to batteries.\textsuperscript{13} Figure 2 shows the basic structure model of electrochemical capacitor. The active material is usually pressed or coated onto the current collector and immersed in the electrolyte. The separator prevents the two electrodes from short-circuiting each other, but is ion-permeable allowing ionic charge transfer to take place.\textsuperscript{20}

Electrochemical capacitors can be explained via two types of charge storage mechanism. The first category is the electrostatics storage of electric energy in which separation of charges occurs in a static double layer at the electrode–electrolyte interface without involving electron transfer process.\textsuperscript{21} In other words, there is no electrochemical reaction occurring on electrodes during charging/discharging processes. The double-layer capacitance is measured using Eq. (1), as mentioned earlier. In contrast, the second category mechanism utilizes the electrochemical storage of electric energy with fast and reversible redox reactions which result in pseudocapacitance. This is accomplished by electrosorption of specifically adsorbed electrolyte ions at the electrode–electrolyte interface and intercalation of electro-active species in the layer lattice.\textsuperscript{22} The pseudocapacitance can be estimated according to Eq. (2):

\[
C_{pc} = q \left( \frac{d\theta}{dV} \right),
\]
where \( q \) is the Faradaic charge required for adsorption/desorption of ions, \( d\theta \) is the change of surface coverage by adsorbed species and \( dV \) is the change of voltage.\(^6\)

The real complete capacitor cell consists of two capacitors in series.\(^{23}\) Assuming that \( C_1 = C_2 = C \) in a symmetric device, the capacitance values of the two electrodes connected in series give rise to the total capacitance following the Eqs. (3) and (4):

\[
\frac{1}{C_T} = \frac{1}{C_1} + \frac{1}{C_2},
\]

\[
C_T = \frac{1}{2} C.
\]

Subsequently, the specific capacitance \( (C_{sp,2E}) \) of a complete cell can be obtained by dividing the capacitance \( (C_T) \) by the combined mass of two-electrode cell \( (2m) \), according to Eq. (5).\(^{24}\)

\[
C_{sp,2E} = \frac{C_T}{2m} = \frac{1}{4} \left( \frac{C}{m} \right).
\]

It should be noted that the specific capacitance corresponding to a single electrode material \( (C_{sp,1E}) \) using three-electrode cell configuration is four times larger than that of two-electrode cell \( (C_{sp,2E}) \) as shown in Eq. (6), contributing significant difference between complete cell and single electrode.\(^{18}\)

\[
C_{sp,1E} = \frac{C}{m} = 4(C_{sp,2E}).
\]

Regarding this significant importance, attention must be given to the specifications of an electrochemical capacitor whether the values are calculated for a complete two-electrode cell or correspond to single electrode measurement. Unless otherwise specifically stated, the capacitance values discussed throughout this review should be based on single electrode material in order to avoid misleading.

A voltage \( (V) \) is built up across the two electrodes when the electrochemical capacitor is charged.\(^{11}\) The maximum energy \( (E) \) stored by this capacitor is directly proportional to its capacitance \( (C) \) and the square of applied voltage \( (V^2) \) according to Eq. (7).\(^{25}\)

\[
E = \frac{1}{2} CV^2.
\]

Devices with aqueous electrolytes have the maximum operating voltage limited at about 1.2 V due to decomposition of water while organic electrolytes and ionic liquid allow wider voltages window up to 3.5 V and 4.5 V, respectively.\(^{26}\)

The power density \( (P) \) of electrochemical capacitors is proportional to the square of applied voltage \( (V^2) \) and is limited by the resistance \( R \), following the Eq. (8)\(^{17}\):

\[
P = \frac{V^2}{4 \times R},
\]

where \( R \) is the equivalent series resistance (ESR) which is comprised of the electrode resistance, electrolyte resistance and resistance due to the diffusion of ions in the electrode porosity. In general, the inner resistance of electrochemical capacitors is much smaller than that of batteries as a result of fast electron/ion transfer as well as rapid combination of charges.\(^{11}\) Therefore, electrochemical capacitors can discharge the electrical energy stored rapidly in order to produce higher power density than in batteries.

From both Eqs. (7) and (8), it is evident that \( V \), \( C \) and \( R \) are the three important parameters affecting the electrochemical performance of electrochemical capacitors. Choice of electrode materials and type of electrolyte determine the operating voltage of the cell which in turn contributes different magnitudes of energy density\(^{26}\) while electrolyte conductivity, the size of electrolyte ions and the porosity of electrode materials are among the key factors affecting on the ESR of the cell, which in turn determine its power output.\(^{14}\) It should be mentioned that both energy and power densities are proportional to the square of voltage, thus, a great number of researches have been conducted and focused on studying highly conductive and stable electrolytes with a wide operating voltage for a variety of applications.\(^{25}\) On top of increasing operating voltage, enhancing capacitance is considered as one of the key approaches in electrochemical capacitor research and development. This can be attained by improving specific capacitance of electrode materials via optimization of electrode structures. In addition to improving voltage and capacitance, reducing ESR of electrochemical capacitors could also bring advantageous effects to performance enhancement. Therefore, contact resistance between electrode particles, a sum of electrode-current collector resistance, resistance due to the diffusion of ions in the electrode porosity and electrolyte resistance should become the major focus to optimize the performance of electrochemical capacitors.
3. Electrolyte

The choice of an electrolyte is particularly important because the amount of energy stored in the cell and how quickly this energy can be released are determined by the thermodynamic stability of the electrolyte employed. As discussed earlier, energy density of electrochemical capacitor is proportional to the squared voltage. Numerous research efforts have been aimed at exploring highly conducting, stable electrolytes with a wider voltage. Generally, three types of electrolytes are currently employed in electrochemical capacitor applications: (i) aqueous electrolyte, (ii) organic electrolyte and (iii) ionic liquid.

In aqueous electrolyte, concentrated electrolytes such as H₂SO₄ and KOH are able to minimize internal resistance and maximize power capability due to excellent ionic conductivity (0.5–1 S/cm) or much lower electrolyte resistivity (1–2 Ω cm). The great number of proton (H⁺) and hydroxide (OH⁻) involved in proton hopping or proton transport explains the higher ionic conductivity in strong acid and alkali, respectively. However, the use of concentrated electrolyte limits the cycle life of electrochemical capacitor and restricts the range of possible electrode materials because most of metal oxides degrade dramatically in concentrated electrolytes. As a result, neutral and mild aqueous electrolytes including KCl, Na₂SO₄, Na₂SO₃ and Li₂SO₄ have therefore been considered for use with metal oxides. Compared with organic electrolytes, aqueous electrolytes exhibit higher capacitance due to relatively smaller ionic size (5 Å to 10 Å) and lower internal resistance. The resistance of electrochemical capacitor is strongly dependent on the conductivity of electrolyte and the size of electrolyte ions which penetrate into and out from the pores of electrode particles. With the same reasons, aqueous electrolytes also tend to produce faster rates of charges and discharge. Additionally, preparation of aqueous electrolytes undergoes less stringent purification and drying processes due to the absence of flammable and toxic solvent. Consequently, the fabrication and material cost of aqueous electrolytes are much lower in comparison to organic electrolytes. However, the main drawback of aqueous electrolytes is their relatively smaller voltage window, which is limited by the electrolysis of water to 1.23 V at 25°C. As can be seen from Eqs. (7) and (8), aqueous electrolytes have limitation in term of enhancing both energy and power densities because of their narrow voltage window. This is the reason why organic electrolytes are often recommended.

Moving from aqueous to organic electrolyte, the voltage window is increased from 1.2 V to 3.5 V. By all means, this is a great advantage of organic over aqueous electrolytes. Typically, the operating voltage is set to 2.5 V to prevent decomposition of the electrolyte through over-charging. In order to ensure that organic electrolytes can operate at higher voltages, an inert atmosphere which is free of water and oxygen is needed to handle these electrolytes. This is because the evolution of H₂ and O₂ gases occurred at the potential difference above 1.23 V. Among organic electrolytes, acetonitrile is the most commonly used solvent. However, its toxicity and flammability require more stringent and costly preparation processes. Organic electrolytes have low conductivity (0.01–0.05 S/cm) which leads to high internal resistance or ESR (20–60Ω cm). The increased viscosity in organic electrolytes also further increases the ESR. The organic ions with relatively larger size (15–20 Å) are more difficult to diffuse into or out of the pores of electrode materials. This results in poorer specific capacitance in organic-based electrochemical capacitors.

Ionic liquids (ILs) are room-temperature liquid solvent-free electrolyte. ILs are essentially molten salts with melting temperatures at or below room temperature. Imidazolium, pyrrolidinium and quaternary ammonium slats are among the most widely studied ILs for electrochemical capacitor applications. The main advantages of using ILs include wide electrochemical stability window up to 6 V, high thermal and chemical stability, low flammability and low vapor pressure. Their voltage window stability is thus only driven by the electrochemical stability of the ions. The ionic conductivity of these liquids at room temperature is very low, so they are mainly used at higher temperature. Unfortunately, ILs have relatively high viscosities and much lower ionic conductivities than aqueous electrolytes. In addition, ILs is hygroscopic which require to be handled in stringent and controlled processes. Another major disadvantage of using ILs is their high cost, restricting the larger scale production.

4. Electrode Materials

As discussed in Sec. 2, capacitance, operating voltage and inner resistance of electrochemical capacitors
are greatly dependent on electrode materials. By further exploring and developing new materials with improved performance relative to current electrode materials in the market is the most effective approach to make electrochemical capacitors become very competitive choices for energy storage applications. In relation to the recent trends of research and development, electrochemical capacitors can be classified into three main categories: (i) EDLCs such as carbon-based materials, (ii) pseudocapacitors including transition metal oxides and conducting polymers and (iii) hybrid capacitors. Carbon-based materials, ranging from ACs to carbon nanotubes (CNTs) and graphene which exhibit static double-layer capacitance via charge separation/accumulation, have become the most extensively examined electrode materials in EDLCs, owing to the large surface area, high electronic conductivity, sufficient chemical stability and low costs. Transition metal oxides, lithium metal oxides and conducting polymers are examples of pseudocapacitors which might be able to contribute up to 10–100 times more than that of EDLCs due to their fast and reversible surface redox reactions. Hybrid capacitors utilize both electrostatic and electrochemical mechanisms to store charge, achieving greater energy and power densities than pure EDLCs or pseudocapacitors. Three different types of hybrid capacitors become the focus of the current research, depending on their electrode configuration: composite, asymmetric and battery-type, respectively. Combination of EDLCs and pseudocapacitors with the latest generation of lithium metal oxide has brought the energy density of electrochemical capacitors closer to that of batteries.

### 4.1. Electric double layer capacitors

Since initial commercialization of electrochemical capacitors in 1978, carbon has been widely used as an electrode material for EDLC. From the substantial amount of published literature available on carbon electrode materials, it is clear that the attraction of carbon as electrochemical capacitor electrode material arises from the distinctive chemical and physical properties, namely, high surface area (\(\sim 100 \text{ to } 2000 \text{ m}^2/\text{g}\)), good corrosion resistance, high temperature stability, controlled pore structure, relatively high conductivity, processability and compatibility in composite materials. On top of the unique combination of chemical and physical properties, great abundance, easy availability and low cost are some of the attractive merit points of carbon for electrochemical capacitor applications. However, carbonaceous compound suffers from the major drawback of high resistivity due to the contact resistance between carbon particles which gives rise to a high internal series resistance. Carbons are available with a specific surface area of up to 2500 m\(^2\)/g in the form of AC, carbon black (CB), carbon aerogel, carbon fiber cloth, powdered graphite, graphite cloth, glassy carbon, CNT and graphene. Among the carbon-based materials, AC, CNT and graphene have been extensively studied.

AC utilizes a complex porous structure composed of differently sized micropores (< 2 nm wide), mesopores (2–50 nm) and macropores (> 50 nm) to achieve high surface area. Based on the storage mechanism of EDLCs, the specific surface area of AC electrode material is directly proportional to the specific capacitance. Theoretically, it is proposed that the higher specific surface areas would strongly correlate to the improved capacitive performance. However, practical situations are more complicated for a wide variety of ACs as this trend is not perfectly followed. Qu and Shi studied the correlation between structural morphology (BET surface area, average pore size, pore size distribution) and capacitive performance of high-surface-area ACs (1370–2371 m\(^2\)/g). The study revealed that the measured capacitance of ACs did not demonstrate a linear relationship with their surface area. With these observations, the authors have identified two primary reasons for the phenomenon. First, a wide variety of ACs made from different types of precursors through activation processes and subsequent treatments yield inconsistent double-layer capacitance. Secondly, not all the Brunauer-Emmett-Teller (BET) surface area is electrochemically accessible when in contact with electrolyte. It is believed that those large solvated ions, which are too big to enter those micropores, contribute to the sieving effect on the total double-layer capacitance. In general, the capacitance values of ACs range from 100 F/g to 200 F/g in aqueous medium, and from 50 F/g to 150 F/g in organic medium. A smaller size of solvated ions and a higher dielectric constant in aqueous electrolyte result in the higher capacitance values. In contrast, organic electrolytes with larger ion sizes which cannot penetrate the pore volume to an equivalent extent, exhibit poorer
capacitive performance. It is proposed that microporous carbon with a high specific surface area is effective for higher energy densities with a relatively slow charge–discharge. On the other hand, in order to obtain higher power densities, carbon electrodes should contain a large amount of mesopores because their relatively larger pore size allows improved ion accessibility and diffusion. Generally, macropores which act as transport pathway into the inner carbon particles, make insignificant contribution to the total surface area of porous carbon. Thus, it has conclusively been shown that the optimized pore size is crucial for high capacitive performance. In summary, specific surface area, morphology, pore size distribution and surface functionalities have become the major areas of research in EDLC design.

CNTs, which were first discovered in 1991, have significantly advanced the science and engineering of carbon materials. With excellent electrical conductivity, high thermal stability and good mechanical integrity, CNTs have been studied to offer a new possibility for carbon electrodes for many applications such as batteries, hydrogen storage, flat panel displays, chemical sensors, etc. In addition, their high accessible surface area, narrow pore size distribution and unique pore structure has also led to CNTs being extensively researched as materials for electrochemical capacitor electrodes. CNTs are used as three-dimensional supports for active materials owing to their unique morphology and extended graphitic layers. With the open mesoporous network formed by the entanglement of nanotubes, the electrodes are able to adapt to the volumetric changes during charging and discharging and the ions diffuse easily to the active surface of the electrode. These properties are essential to improve the cycling performance and enhance the power density of the device. CNTs are generally observed in one of the two forms, multiwalled or single-walled, which were found in 1991 and 1993, respectively. Single-walled carbon nanotubes (SWNTs) have cylindrical walls with diameters ranging between 1 nm and 3 nm. SWNT consists of a one-atom thick layer of graphite or better known as graphene wrapped into a seamless cylinder while the configuration of multiwalled carbon nanotubes (MWNTs) can be visualized as multiple rolled layers of graphene separated by a single-layer-graphene spacing (~0.34 nm). The first reported MWNT electrochemical capacitor electrodes have been prepared by Niu et al., showing specific capacitance of 113 F/g in H2SO4 solution. Frackowiak et al. investigated the electrochemical characteristics of MWNT pellet electrode with the maximum specific capacitance of 135 F/g in 6 M KOH. It is noteworthy that recent studies have shown that entangled CNTs are less efficient in facilitating fast ionic transportation in comparison to aligned CNTs as a result of the irregular pore structures and high entanglement of the CNT structure in the former electrode. Therefore, the use of aligned CNT would be more beneficial for enhancing rate capability and energy density of electrochemical capacitors. A densely packed aligned SWNT solid was first fabricated by Futaba et al. by using the zipping effect of liquids, which allowed the bulk materials to retain the intrinsic properties of SWNTs. In spite of having excellent properties, high manufacturing cost has restricted the use of CNTs as bulk active material in EDLC electrodes. Therefore, the recent developments for the use of CNTs in electrochemical capacitor applications are as conductivity enhancers which replace CB. The study on changing acetylene black (AB) to CNTs in EDLC electrodes resulted in a 90% reduction in ESR.

In recent years, a considerable attention has been shifted from AC and CNT to graphene in making composite electrodes due to its good conductivity, superior chemical stability, high elastic and mechanical strength, large surface area, suitable pore size distribution and rapid heterogeneous electron transfer. Graphene, which was discovered by Geim’s group in 2004, is a single layer of carbon atoms densely packed into a honeycomb structure. Since Vivekchand et al. and Stoller et al. pioneered graphene-based electrochemical capacitors, these unique and novel materials have been extensively investigated as possible electrodes for electrochemical energy storage device applications. Unlike the current electrochemical capacitors fabricated with AC and CNT, the high effective specific surface area of graphene does not depend on the distribution of pores. The effective surface area of graphene materials is dependent highly on the layers, that is, single or few layered graphene, which have a lower degree of agglomeration. In most recent reports, the chemically modified graphene sheets have demonstrated a very large surface area which is fully accessible to the electrolyte ions while maintaining the high electrical conductivity and good mechanical properties. Recently, Wang and...
co-workers have successfully fabricated the graphene-based electrochemical capacitor that exhibit remarkable results with specific capacitance of 205 F/g, energy density of 28.5 Wh/kg and power density of 10 kW/kg in KOH aqueous solution.\(^\text{31}\) These outstanding findings prove that graphene-based electrochemical capacitors exceeded the specific energy of 21.4–42.8 Wh/kg, which is comparable to that of a modern nickel metal hydride battery used in a hybrid vehicle.\(^\text{32}\) An interesting phenomenon was observed by Cheng et al. after charging and discharging graphene electrode galvanostatically for about 1300 cycles in 1 M KCl.\(^\text{43}\) Surprisingly, the specific capacitance increased significantly instead of degrading as seen in typical cycling trend of electrochemical capacitors. Authors claimed this observation as electro-activation of graphene sheets in which long charging–discharging process may help electrolyte ions intercalate into the spaces between graphene layers, fully utilizing the effective surface area of electrode materials. CV curves after about 1300 cycles also revealed that the specific capacitance of 245 F/g is much higher than those of CNT-based electrodes because graphene nanosheets can adapt different sizes of electrolyte ion by physical sheet movement.

### 4.2. Pseudocapacitors

RuO\(_2\) in either a crystalline or amorphous hydrous form have been studied extensively in acidic solutions in the past 30 years because of their high specific capacitance and high conductivity characteristics.\(^\text{25}\) In 1971, Trasatti and Buzzanca firstly used RuO\(_2\) as electrochemical capacitor electrodes in aqueous H\(_2\)SO\(_4\). They recognized that the capacitive performance is attributed to a successive electron transfer at redox active sites (Ru\(^{2+}\), Ru\(^{3+}\), Ru\(^{4+}\)), balanced by the proton transfer which leads to the conversion of O\(^{2-}\) to O\(^{-}\) sites in the oxide structure.\(^\text{44}\) Similarly, Lokhande and co-workers (2010) have identified that the electron transfer between and within the RuO\(_2\) particles, electron hopping between the particles and current collectors and proton diffusion within RuO\(_2\) particles are the primary factors affecting the capacitive performance of hydrous RuO\(_2\).\(^\text{45}\) Although crystallization of RuO\(_2\) can reduce the intraparticle electron hopping resistance of RuO\(_2\)-nH\(_2\)O particles, Gujar and co-workers claimed that the crystalline nature of RuO\(_2\) electrodes limits capacitive performance through an increase in the diffusion barrier of proton within the rigid lattice of crystalline structure.\(^\text{46}\) In fact, literature survey of electrochemical capacitors shows that recent research focuses on amorphous hydrous RuO\(_x\)-nH\(_2\)O thin film-based electrochemical capacitor via various methods including sol–gel, cyclic voltammetric deposition, anodic deposition, spray deposition, hydrothermal synthesis, oxidative synthesis, etc.\(^\text{46,47}\) The advantages of amorphous hydrous ruthenium oxides (RuO\(_x\)-nH\(_2\)O) include high specific capacitance, high conductivity and good electrochemical reversibility.\(^\text{48}\) As reported in a literature,\(^\text{49}\) hydrous RuO\(_2\)-0.5H\(_2\)O exhibits high capacitance value (~900 F/g). However, the capacitance decreased to 29 F/g when the water content was reduced to RuO\(_2\)-0.3H\(_2\)O. Most of the review articles of RuO\(_2\)-based electrochemical capacitors have focused on the capacitive performance of electrodes mainly in the concentrated sulfuric acid (H\(_2\)SO\(_4\)).\(^\text{45}\) Some researchers claimed that conducting metal oxides such as RuO\(_2\) are only suitable for aqueous electrolytes, suggesting that high capacitance value and fast charging are the pseudocapacitance contribution from surface reaction between Ru ions and protons (H\(^+\)). Hence, a strong acid is therefore necessary to provide good ionic conductivity.\(^\text{28}\) However, it should be noted that the cycling performance of metal oxide electrodes will be deteriorated because electrodes tend to dissolve rapidly in the highly concentrated acidic electrolyte.\(^\text{50}\)

There has been an increasing interest in MnO\(_2\)-based electrode for energy storage applications because of its cost effectiveness and low toxicity in comparison to other metal oxides such as RuO\(_2\), NiO and CoO\(_2\).\(^\text{51}\) In general, the pseudocapacitance of MnO\(_x\) is believed to be predominantly attributed to the redox transitions associated between Mn (III/Mn(II), Mn(IV)/Mn(III) and Mn(VI)/Mn (IV)).\(^\text{52}\) In comparison to the studies of RuO\(_2\)-based electrochemical capacitor, milder aqueous solutions such as KCl and Na\(_2\)SO\(_4\) have therefore been adopted for MnO\(_2\) electrode.\(^\text{45}\) The first study on Faradaic pseudocapacitive behavior of nano MnO\(_2\) by Lee and Goodenough has shown that mild KCl aqueous solution can replace strong acid such as H\(_2\)SO\(_4\) as the electrolyte of electrochemical capacitor.\(^\text{53}\) Based on the experiment, the electrode materials containing amorphous MnO\(_x\)-nH\(_2\)O and AB showed a specific capacitance of 200 F/g.\(^\text{53}\) Typically, thick films of MnO\(_2\) yield the specific
capacitance values range from 125 F/g to 250 F/g.\(^{51}\) Conversely, ultrathin MnO\(_2\) film electrodes exhibit excellent specific capacitance which could be due to the fact that the thinner films possess considerable lower contact resistance between film matrix and current collector.\(^{54}\) On top of that, thin films could provide a shorter proton diffusion path length. Pang \textit{et al.} has demonstrated a specific capacitance of 700 F/g for very thin MnO\(_2\) films prepared by sol–gel techniques.\(^{54}\) Broughton and Brett also have observed a specific capacitance of 700 F/g in thin MnO\(_2\) films prepared by anodic oxidation.\(^{55}\) Obviously, in comparison to thin-film electrodes, the capacitance of thick MnO\(_2\) electrodes is ultimately limited by the poor electrical conductivity of MnO\(_2\).\(^{56}\)

Nickel oxide (NiO) is being considered as one of the promising potential electrode materials for electrochemical capacitors with an anticipation that it could serve as a low-cost alternative of noble oxide RuO\(_2\)-based electrochemical capacitor, owing to its easy availability, environmental benign nature and cost effectiveness.\(^{57}\) Nickel becomes the primary material in alkaline batteries including nickel-metal hydride and nickel-cadmium batteries as a result of the formation of protective oxide/hydroxide surface in alkaline electrolytes.\(^{58}\) Wu \textit{et al.} demonstrated the comparative studies on the deposited NiO film in 1 M KOH and 1 M Na\(_2\)SO\(_4\) solutions, respectively.\(^{59}\) The authors claimed that the redox between NiO and OH\(^{-}\) results in high capacitance of NiO in alkaline solution. In contrast, no significant peaks were observed for the deposited nickel oxide film in 1 M Na\(_2\)SO\(_4\) solution, suggesting that the solution has a much lower concentration of OH\(^{-}\) in comparison to 1 M KOH solution. Consequently, the capacitive performance in Na\(_2\)SO\(_4\) solution mainly comes from the double-layer effect of the deposited nickel oxide film. Recently, Wu \textit{et al.} have successfully synthesized the porous nickel oxide film with interconnected nanoflakes and open macro pores by anodic electrodeposition.\(^{60}\) The nanoflakes are believed to be beneficial for the capacitance enhancement of NiO due to their high surface area and shortened diffusion path in solid phase. On top of the nanoflakes, a porous film with open macro pores also provides a pathway to aid the electrolyte ion penetration into the interior oxide, facilitating the electrolyte ion penetration, leading to an increase in specific capacitance of NiO (351 F/g).\(^{61}\)

Fe\(_3\)O\(_4\) has been identified as potential electrode material in view of the low-cost and environmentally friendly nature.\(^{61}\) The preliminary evaluations revealed that the relatively low electrical conductivity of Fe\(_3\)O\(_4\) requires the introduction of conductive additive such as CB and AB in order to increase its conductivity and boost its capacitance.\(^{62}\) Wu and his co-workers first compared the capacitive performance of Fe\(_3\)O\(_4\)-CB electrodes showing the specific capacitance of 38 F/g in sodium sulfite (Na\(_2\)SO\(_3\)).\(^{62}\) Similarly, Brousse and Belanger synthesized Fe\(_3\)O\(_4\) nanopowders with high surface area (115 m\(^2\)/g) and reported a specific capacitance value of about 75 F/g in 0.1 M K\(_2\)SO\(_4\).\(^{27}\) Wang \textit{et al.} investigated the capacitance mechanism of electroplated Fe\(_3\)O\(_4\) thin-film electrodes in Na\(_2\)SO\(_3\), Na\(_2\)SO\(_4\) and KOH aqueous solutions.\(^{63}\) Experimental results indicate that Fe\(_3\)O\(_4\) electrodes in Na\(_2\)SO\(_3\) exhibit highest specific capacitance value (170 F/g), followed by Na\(_2\)SO\(_4\) (25 F/g) and KOH (3 F/g). The authors suggested that significant improvement on the capacitive performance in Na\(_2\)SO\(_3\) is attributed from the synergy effect of both EDLC and the pseudocapacitance which involves successive reduction of the adsorbed sulfite anions. In contrast, the capacitive current is attributed to EDLC only in Na\(_2\)SO\(_4\). In recent years, cathodic electrodeposition method has been developed for the fabrication of iron oxide films, containing chitosan additive as a binder.\(^{64}\) The iron oxide films exhibited specific capacitance as high as 210 F/g in 0.25 M Na\(_2\)SO\(_3\) solution. It is claimed that the capacitive performance of Fe\(_3\)O\(_4\) is heavily dependent on the nature of anions and the surface area of electrodes.\(^{27,62,63}\)

Conducting polymers can offer relatively cost-effective alternative to the conventional electrode materials as a result of their fast doping/dedoping capabilities, excellent electrochemical reversibilities and high conductivity in a doped state.\(^{65}\) Nevertheless, the poor power density caused by the slow diffusion of electrolyte ions within the entire electrode becomes the main disadvantage of conducting polymers.\(^{69}\) In addition, conducting polymer-based electrochemical capacitors exhibit lower cycle life due to volume change or swelling as a result of the doping (intercalation)/de-doping (de-intercalation) of ions.\(^{67}\) The conductivity of conducting polymer was first reported in 1963 by McNeill and co-workers.\(^{65}\) They exhibit the pseudocapacitive and conductive behavior via electron delocalization in conjugated chemical bond system along the polymer backbone. Among various conducting polymers, polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh),
poly (3, 4-ethylenedioxythiophene) (PEDOT) and poly(styrene sulfonate) (PSS) are most commonly studied for use in electrochemical capacitors. The experimental specific capacitance values of PANI, PPy and PEDOT are 240, 530 and 92, respectively.

4.3. Hybrid capacitors

Most recently, major research efforts are focused on exploring new materials to improve energy density of electrochemical capacitors. Particularly, increasing both capacitance and operating voltage of electrochemical capacitors are of significant importance since energy density is proportional to capacitance and squared voltage. With these reasons, three main approaches are proposed: (i) replacing electrode material with higher capacitance nanostructured carbon or pseudocapacitive materials, (ii) changing electrolyte by durable new electrolytes and (iii) developing hybrid cell configurations. In particular, exploring new hybrid energy storage systems have received a great deal of attention. The possible hybrid cell configuration is the combination of EDLCs and pseudocapacitive materials which offers synergistic effect in capacitive performance. It can be observed from Fig. 3, that the most widely investigated metal oxide is ruthenium oxide because of its excellent pseudocapacitive behavior, good reversibility and high conductivity. However, the high cost of this precious metal oxide hinders its practical applications. Consequently, relatively low-cost materials such as MnO₂, NiO, Fe₃O₄, ZnO, TiO₂, etc. have been explored as possible composite electrode materials for electrochemical capacitors working in aqueous solution.

4.3.1. Ruthenium oxide (RuO₂)-based composites

RuO₂ is widely studied because it is conductive and has three accessible distinct oxidation states. The pseudo-capacitive behavior of RuO₂ in acidic solutions has been the focus of research in the past 30 years. In order to reduce the cost of materials while maintaining its high charge storage performance, extensive works have focused on the development of combining RuO₂ with carbonaceous materials to form bulk composite electrodes. The study of RuO₂/AC nanocomposites with various Ru contents in 1 M H₂SO₄ was reported by Kim and Popov respectively. The results revealed that when Ru content increases, the specific capacitance and BET surface area of the composites decrease gradually. This is mainly due to the blockage of the mesopores in AC by large RuO₂ particles. The 40 wt.% RuO₂ loaded composite electrode showed the most effective composition with the highest energy density (17.6 Wh/kg) and material cost reduction. The high RuO₂ loading of 80 wt.% exhibited very poor rate capability because the large RuO₂ particles that accumulated on the carbon surface blocked most of the pores. In the study of the capacitive performance for hydrous RuO₂/mesoporous carbon composite electrodes, Jang et al. (2003) addressed that the unloaded mesoporous carbon exhibited a specific capacitance of 100 F/g,
but increases to 243 F/g with 54.3 wt.% RuO₂ loading in 2 M H₂SO₄. It should be pointed out that, the capacitance increase with ruthenium loading is likely counterbalanced by a loss of rate capability. An increase in the ohmic voltage drop or ESR, with increase in RuO₂ loading is verified by galvanostatic charging–discharging measurements. The possible explanation of the ESR enlargement with increasing RuO₂ loading is that the hindered ionic motion which is caused by a pore narrowing has increased the electrolyte resistance within the narrowed pores.

In Liu Zhang’s work, small amount of RuO₂ was successfully incorporated into NiO-based electrode to improve the low capacitance and energy density of NiO electrochemical capacitor. By adding 10 wt.% RuO₂ into NiO-based electrode, a high specific capacitance of 210 F/g is obtained for the composite electrode in 1 M KOH. Additionally, the energy density of the NiO/RuO₂ composite electrode is enhanced from 2.6 Wh/kg (pure NiO electrode) to 14.2 Wh/kg. It is believed that the incorporation of RuO₂ into the composite electrode has extended the operating voltage. Figure 4 shows the impedance spectra of NiO/RuO₂ composite electrode and pure NiO electrode. It can be seen that the semicircle of NiO/RuO₂ composite electrode is smaller than that of pure NiO electrode, indicating that the presence of conductive RuO₂ has improved the charge-transfer resistance of the composite electrode. Ahn et al. found that the electrochemical performance of the RuO₂-based electrodes can be improved by adding the TiO₂ nanorods which are further heat treated at 800 °C under nitrogen. In addition, the capacitive performance of RuO₂/TiO₂ nanotubes is found to be significantly enhanced, mainly attributed to the highly accessible surface areas of RuO₂. The loading of RuO₂ in TiO₂ nanotubes can improve the proton interaction with RuO₂, which in turn promote the electrochemical capacitor performance and the cyclic stability.

4.3.2. Manganese oxide (MnO₂)-based composites

MnO₂ is the second extensively studied electrode materials after RuO₂ because of its low cost and environmental friendly nature. However, the capacitive performance and power characteristics of MnO₂ electrode are limited by its poor conductivity. Introduction of conductive, porous and high surface area carbon-based materials is a feasible route to enhance the charge-storage capability by shortening electron transport distance. The research which focused on MnO₂/CNT nanocomposites showed good capacitive behavior, with the highest specific capacitance of 356 F/g in 0.5 M Na₂SO₄. The results indicated that the samples containing CNT showed significantly lower resistance compared to the sample without CNT, suggesting that the porous microstructure of CNTs has facilitated the access of electrolyte ions to the active material. Cheng and co-workers have successfully fabricated electrochemical capacitors using MnO₂-coated graphene to provide a high specific capacitance of 328 F/g and energy density of 11.4 Wh/kg in 1 M KCl. The access of electrolyte ions to high-surface area graphenes are enhanced due to the physical adjustment of nanosheets between graphene materials. In addition to the ideal structure of graphene for ion adsorption, the MnO₂ nanoparticles grown on the graphenes also help increase the distance between nanosheets in order to accommodate more electrolyte ions.

The incorporation of other metal elements such as lead (Pb) and iron (Fe), onto the MnO₂-based electrodes was found to further improve the electronic conductivity and charge-storage capability of the composite electrodes by introducing more defects and charge carriers via the doping process. It should be noted that the amount of metal additives has significant effect on the capacitive performance of the composite electrodes. The MnO₂-based electrode with the addition of 20% Pb has increased the specific capacitance of MnO₂ electrode from 166 F/g to 185 F/g. The observed capacitance enhancement can be explained by the increased surface area of the composite electrodes due to the
formation of micropores. Lee et al. conducted a study on the effect of Fe addition upon capacitive behavior of MnO₂-based electrode, suggesting that the addition of 0.05 M FeCl₃ exhibited optimum specific capacitance of 212 F/g. The authors also revealed that the Fe addition significantly affects the surface morphology of the MnO₂ electrodes, as shown in Fig. 5. As seen from the SEM images, surface roughness of the deposited oxides gradually increases with increasing FeCl₃ concentration in the plating solution up to 0.05 M. However, after which, the surface began to be smoother as the FeCl₃ addition was further increased. It is noteworthy that cracks observed on the surfaces of all the deposited oxides were probably caused by shrinkage stress during drying. Another novel design of MnO₂/Mn/MnO₂ triple-layered structure has been successfully developed by Li et al., exhibiting very high specific capacitance of 937 F/g with excellent cycling stability up to 300 cycles in 1 M Na₂SO₄. It is suggested that the unique architectures of the highly conductive Mn layer and the double hallow nanostructured MnO₂ have provided large surface area and short ion diffusion path that contribute to the high capacitive performance.

On top of their poor electronic conductivity, the electrochemical cyclability is another important issue for MnO₂ electrodes. Zhang et al. achieved promising result from MnO₂/PANI composites with the maximum specific capacitance of 320 F/g compared to that of pure MnO₂ (125 F/g). In addition, the specific capacitance retains approximately 84% of the initial value after 10,000 cycles, indicating the good cycle stability of the composite electrode. With excellent conductivity and mechanical stability, PANI polymers enable enhanced electrochemical and mechanical properties of the composites. Another study on MnO₂-based electrode with the addition of PPy showed the improved specific capacitance of the MnO₂-PPy nanocomposite (290 F/g) compared to that of pure MnO₂ electrode (221 F/g). The enhancement is attributed to a combination of the improved conductivity effect and the high specific capacitance of PPy. Mesoporous MnO₂/PANI composite with unique morphology via interfacial synthesis has been synthesized successfully by Wang et al. This amorphous composite electrode exhibits higher surface area and more uniform pore-size distribution compared to MnO₂/PANI composites prepared by chemical co-precipitation. These findings reveal that the well-defined mesoporous microstructure processes reduced diffusion length path, allowing faster diffusion of electrolyte ions into the uniform mesopores.

4.3.3. Nickel oxide (NiO)-based composites
NiO is one of the most widely investigated metal oxides for electrochemical capacitor applications due to its pseudocapacitive and highly electronic conductive behavior. Yuan et al. studied the electrochemical behavior of AC loaded with NiO. It is somewhat surprising that although the BET surface area was decreased from 1332 m²/g to 1232 m²/g by the loading of 4 wt.% NiO onto AC, the capacitance was increased from 175 F/g to 194 F/g. A possible explanation for this might be that the decreased BET surface area is compensated by the pseudocapacitance contribution from the redox reaction of NiO in NiO/AC composite electrodes. Another study on the NiO/CNT nanocomposite in 2 M KOH showed that the incorporation of 10 wt.% CNTs improves the capacity up to 160 F/g, revealing the

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Fig. 5. Surface morphologies of the oxides deposited in the MnO₂ with addition of (a) 0, (b) 0.03, (c) 0.05, (d) 0.06, (e) 0.08 and (f) 0.15 M FeCl₃.
large surface area of CNT acts as the active sites for Faradaic reaction of NiO. Additionally, the formation of conducting CNT networks in NiO significantly enhances the electrical conductivity of the composite electrodes. In should be noted that, in comparison to the CV curves obtained from the three-electrode electrochemical measurement on nanostructured NiO in Ref. 78, the CV curves of both pure NiO and NiO/CNT measured from two-electrode cell show no current peaks and nearly symmetric shape (Fig. 6). NiO/CNT nanocomposite electrode which reveals that more rectangular shape is closer to an ideal capacitive material as compared to that of pure NiO. A composite electrode that consisted of MnO2/NiO mixed oxides were successfully prepared by Kim and Popov and the electrode was exhibiting specific capacitance of 172 F/g with the addition of 20 wt.% carbon acting as conductive additives. Recent research has also been undertaken to improve specific capacitance of CNT electrodes by modification of CNTs with pseudocapacitive materials such as metal oxides and conducting polymers via Faradaic processes.

4.3.4. Iron oxide (Fe3O4)-based composites

In view of low cost, low environmental impact and relatively high theoretical capacity previously demonstrated in Li-ion batteries, iron oxide-based composites have been proposed to have great potential for large-scale applications. Wu firstly reported that Fe3O4-SnO2 composite electrode in 1.0 M Na2SO4 aqueous solution can achieve a specific capacitance of 33 F/g using two-electrode measurement. It is suggested that the low conductivity of Fe3O4 combined with other conductive materials such as SnO2 is essential to obtain large capacitance. However, the main weakness of the study is that the failure to address the optimal loading of SnO2 nanopowders into the Fe3O4 electrodes. In 2010, B. Sassin et al. utilized the electroless deposition method to fabricate nanoscale iron oxide coating onto carbon nanofoams. The resulting iron oxide-carbon nanofoams composite electrodes demonstrated high specific capacitance (85 F/g) relative to the pure carbon nanofoam (31 F/g) in 2.5 M Li2SO4. It is believed that the additional charge-storage capacity arises from Faradaic pseudocapacitance of the iron oxide coating. A composite electrochemical capacitor containing Fe3O4 nanoparticles dispersed in MWNTs was reported by Park and Kim. The Fe3O4-MWNTs composite electrode exhibits specific capacitance of 165 F/g in 1 M Na2SO4, which is almost three-fold enhancement compared to the pure MWNT electrode (58 F/g). In the work by Pang et al., they reported the capacitive characteristic of Fe3O4/carbon nanocomposite thin film in 1 M Na2SO4 solution. In their study, sago starch is chosen as the carbon source as well as a surfactant to control aggregation of Fe3O4 nanoparticles and the effect of calcination temperature on the specific capacitance of the nanocomposites was investigated. Figure 7 shows that the specific capacitance increases substantially with increasing calcination temperatures up to 300°C but starts to decrease to above 300°C. The maximum specific capacitance (124 F/g) is obtained for the nanocomposites which exhibit the highest specific area at 300°C. It is thus believed that the densification of films up to 300°C could lead to enhanced electronic conductivity. However, the reduction in specific capacitance at above 300°C could be attributed to the reduction in total surface area caused by grain coarsening. These findings support the earlier observation by Wu which found...

![Fig. 6. CV curves of (a) pure NiO and (b) NiO/CNT measured from two-electrode cell show no current peaks.](image-url)
the similar trend of the correlation between the calcination temperature and the capacitance of SnO$_2$ electrodes. The author explained that the rise in the capacitance of the SnO$_2$ electrodes with increasing calcination temperature is attributed to the reduction in defect density and an increase of crystallinity. This explanation is consistent with the Mott–Schottky relationship which predicts an increase in interfacial capacitance with increasing of the carrier density of the semiconductor.

4.3.5. Zinc oxide (ZnO)-based composites

ZnO has received a great deal of attention in the application of electronics and optoelectronics such as battery active materials, solar cells, gas sensors and light-emitting diodes due to its good electrochemical activity, well-known surface conductivity, high electron mobility, wide bandgap and eco-friendly nature. However, zinc oxides have a serious drawback on the formation of dendrite growth during consecutive cycling which leads to decrease in cycle life. With a view to improve both capacitive and cycling performances of ZnO, Selvakumar et al. studied the electrochemical performance of ZnO/AC composite materials in 0.1 M Na$_2$SO$_4$ as the electrolyte. The ZnO/AC nanocomposite electrode showed a specific capacitance of 160 F/g. The specific capacitance of the electrodes decreased with the increasing of ZnO content. These findings also support the idea that there is a synergistic effect from ZnO and carbon materials in controlling the dendrite formation and thus maintaining stable specific capacitance of composite electrodes.

A comparative evaluation of ZnO/carbon with pure ZnO showed that the removal of carbon reduced the specific capacitance from 21.7 F/g to 7.38 F/g, indicating the significant role of carbon in enhancing the capacitance. These findings suggested that cations and anions from metal oxides and aqueous electrolyte such as Zn$^{2+}$, Na$^+$, K$^+$, H$^+$, SO$_4^{2-}$ and OH$^-$ can occupy some pores within the high-surface-area carbon electrodes and then participate in the formation of the electrochemical double layer. Another group has developed ZnO/CNT electrochemical capacitor cells that achieved a high capacitance of 324 F/g. The study showed that the capacitance of CNT-ZnO is higher than that of pure CNT cells in 1 M KCl aqueous electrolyte. The presence of ZnO is the main cause in the increase of the total capacitance as the redox reactions occur on the composite electrode/electrolyte interface through the electrochemical conversion of Zn$^{2+}$ to other valence states. However, the large amount of ZnO accumulated in the network structure of CNT matrix lowers the specific surface area of CNTs and thus decreases the adsorption of charge carriers such as protons and electrons on the surface of the electrodes. Lu and co-workers have developed ZnO/graphene in 1 M KCl for electrochemical capacitor applications. The specific capacitances of ZnO/graphene and graphene electrodes that were calculated from the study are 62 F/g and 39 F/g, respectively. The EIS conducted on ZnO/graphene, SnO$_2$/graphene and pure graphene electrodes shows that pure graphene electrode exhibited the highest charge-transfer resistance (2.5 $\Omega$), followed by SnO$_2$/graphene (1.5 $\Omega$) and ZnO/graphene (0.6 $\Omega$) (Fig. 8). These comparative
results showed that the ZnO/graphene composite electrodes exhibit better capacitive performance compared to the pure graphene and SnO2/graphene electrodes.

4.3.6. Titanium oxide (TiO2)-based composites

TiO2 is considered as an environment friendly n-type metal oxide semiconductor because it can be utilized to decompose harmful organic and inorganic pollutants that are present in air and aqueous system under sunlight or indoor fluorescent irradiation. However, the poor conductivity of TiO2 restricts its application as electrode material for electrochemical capacitors (EC) application. Although TiO2 nanomaterials are not suitable to be used as the core electrode material for EC, many research studies revealed that it can enhance the homogeneity of other metal oxides or hydrous oxide within the electrode mixture. It is important to control the dispersion behavior of fine particles in various solvents in the field of electrochemical capacitor because the dispersibility of fine particles affects the electrochemical performance of the charge storage devices. Therefore, several researchers have used TiO2 nanotubes as a solid support to improve the dispersibility of some metal oxides including RuO2 as the pseudocapacitor electrodes. Very recently, Seo and Park conducted a study on the effect of nanosized TiO2 on the electrochemical characteristics of AC electrodes in 1 M H2SO4. Figure 9 demonstrates the effect on the specific capacitance of TiO2/AC composite electrodes with various compositions of TiO2. The optimized content of TiO2 in the composites is found to be 10 wt.%, in which the specific capacitance of the composite electrode has been improved from 100 F/g to 155 F/g compared to that of pure AC electrode.

AC electrodes are polarizable and thus could lead to the reduction of ions accumulation on the double layer. The polarization of AC can be reduced through the modification with nanosized TiO2 since there are more charges on the surface of TiO2 than other regions, as a result of the attractive contribution of positively charged depletion region. It is believed that the improved capacitance of EDLC is attained if the ion concentration on the double layer of AC is increased. This is because some of the AC pores are likely to be filled by hydrox TiO2 after impregnation with TiO2 and thus reduce the polarization of AC. In 2012, Selvakumar and Bhat successfully prepared nanostructured TiO2:AC composite electrodes in three different compositions of 1:1, 1:2 and 1:3 by using microwave-assisted approach. The Nyquist plot for these three different composite electrodes in 1 M Na2SO4, indicating that the charge transfer resistance (size of semicircle) of the composite electrodes was estimated to be about 70 Ω, 50 Ω and 20 Ω for 1:1, 1:2 and 1:3, respectively. The observed highest capacitance (92 F/g) was achieved for the electrode with 1:3 composition.

4.3.7. Cobalt oxide (CoOx)-based composites

Co3O4 materials have the main drawback of poor cyclability as a result of large volume expansion/contraction which could be overcome by coupling Co3O4 nanoparticles with graphene in 6 M KOH. The study revealed that the specific capacitance of 415 F/g was attained when Co3O4 nanoparticles intercalated into the spaces within graphene nanosheets, keeping the sheets from restacking while maintaining their high effective surface area. Similarly, another study on the graphene/Co3O4 nanocomposite in 6 M KOH exhibited specific capacitance of 243 F/g and 95.6% capacitance retention after 2000 cycles, indicating graphene not only acts as a conductive agent but also as a buffer to prevent the volume change in Co3O4 electrodes. A novel system consisting of conductive carbon fiber paper coated with Co3O4 nanowire network demonstrates high specific capacitance (1124 F/g) with remarkable durability up to 5000 cycles. Obviously, such unique electrode design has facilitated stress relaxation during cycling and enhanced ion/electron diffusion.

Fig. 9. Total specific capacitance of TiO2/AC composite electrodes as a function of TiO2 content in 1 M H2SO4.
with improved kinetics of redox reactions. The authors suggested that the similar concept is possibly applied on MnO$_2$ and V$_2$O$_5$ for high-performance electrode materials. Another new approach of designing superior pseudocapacitive nanocomposites composed of mesoporous CoO nanowire with highly conductive conducting polymer PPy, has successfully demonstrated outstanding specific capacitance (2223 F/g) and excellent cycleability (~20000 times).

4.3.8. Other metal oxide-based composites

Many other metals oxides such as copper oxide (CuO), tin oxide (SnO$_2$), molybdenum oxide (MoO$_3$), chromium oxide (CrO$_3$), lead oxide (PbO) and tungsten oxide (W$_{18}$O$_{49}$), have been explored as potential composite electrode materials. Kim and co-workers have prepared CuO/CNT composites which exhibit 60 F/g in 6 M KOH. However, the authors did not indicate the electrochemical results obtained by using two-electrode or three-electrode measurements. In general, specific capacitance calculated from a two-electrode cell is less than half of that obtained from a three-electrode cell, as discussed in Sec. 2. Graphene/SnO$_2$ composite electrodes were prepared by screen-printing approach showing the capacitance value of 42.7 F/g in 1 M KCl. Hu and co-workers (2008) demonstrated that the complementary properties of SnO$_2$ nanoparticles embedded within PANI exhibited excellent capacitance of 305 F/g with a specific energy density of 42 Wh/kg. The enhancement of the capacitive performance is suggested to be attributed to the presence of SnO$_2$ nanoparticles embedded within PANI chains, increasing the electrode–electrolyte interfacial area for insertion and extraction of ions. Very recently, Kang and co-workers adopted a facile approach of electrochemical polarization to fabricate the low-cost nanoporous Ni-Mn based oxy-hydroxide in 1 M (NH$_4$)$_2$SO$_4$ solution, paving new way for the next generation of high-performance EC.

Sugimoto and co-workers first investigated MoO$_3$/AC composite electrodes in 1 M NaOH and 0.5 M H$_2$SO$_4$, respectively. The study demonstrated that an increase in specific capacitance from 132 F/g to 177 F/g was obtained when adding 1.4 wt.% MoO$_3$ onto AC in 1 M NaOH. In 0.5 M H$_2$SO$_4$, this composite electrode exhibits 176 F/g, which is 29% higher than that of AC (136 F/g) with 0.85 wt.% MoO$_3$ loading. Very recently, Aravinda et al. have successfully deposited MoO$_3$ on MWCNTs using magnetron sputtering method. There nanocomposite electrodes exhibit the specific capacitance of 70 F/g in 1 M Na$_2$SO$_4$, measured with two-electrode configuration. The specific capacitance was almost constant up to 800 cycles and decreased to 82% gradually from its initial value at the end of 1000th cycle. Lota et al. have studied the electrochemical performance of CrO$_3$/SWNT in 1 M H$_2$SO$_4$ and 6 M KOH, respectively using two-electrode measurement. These composite electrodes exhibit better capacitive behavior in acidic electrolyte (~50 F/g) than in alkaline solution. A nearly good shape of CV curve of CrO$_3$/SWNT composite electrode 1 M H$_2$SO$_4$ (Fig. 10) shows no redox peaks, explaining that redox transformation of chromium compounds responsible for Faradaic reactions could not be predicted in two-electrode cell measurement. Similar implication was made by Stroller and Ruoff when they reviewed the test methods of both two- and three-electrode cells.

Recently, the investigation on PbO$_2$/AC hybrid capacitor has been carried out using two-electrode cell configuration in 5.3 M H$_2$SO$_4$. The study shows the specific capacitance of 101 F/g and the excellent stability of this hybrid capacitor in concentrated H$_2$SO$_4$ after 2600 cycles. Tian and co-workers have reported a novel smart electrochemical capacitor which delivers new functionalities compared to conventional energy storage devices, employing W$_{18}$O$_{49}$ and conducting polymer PANI as composite materials that is able to display multiple color change in response to varying levels of stored energy in aqueous solution of H$_2$SO$_4$. As can be seen from Fig. 10, the capacitive performance of CrO$_3$/SWNT and pure SWNT electrodes is very similar, but the introduction of CrO$_3$ nanoparticles significantly increases the capacitance.

![Fig. 10. Capacitance calculated from CV curves of CrO$_3$/SWNTs and pure SWNT-based electrodes carried out in 1 M H$_2$SO$_4$ using two-electrode measurement.](Image)
shown from Fig. 11, when the smart composite electrode is fully charged to 0.8 V, the logo on the electrode (SINANO) is transparent on the blue background. On contrary, the logo becomes blue in color on a transparent background as the electrochemical capacitor is discharged at \( \frac{1}{2} \text{C}_0 \). These additional features have brought an important breakthrough in next generation of energy storage technology.\(^{134}\)

4.3.9. Ternary composites

Electron conductivity and mechanical stability of electrode material have always been limitations that hinder the practical applications of EC.\(^{106}\) To overcome these problems, combination of three components in a single electrode material has been attempted recently. A comparative evaluation on nano SnO\(_2\)–Al\(_2\)O\(_3\), SnO\(_2\)–Al\(_2\)O\(_3\)–carbon and SnO\(_2\)–V\(_2\)O\(_5\)–CNT composites were conducted by Jayalakshmi et al. for electrochemical capacitor applications.\(^{107}\) The study showed that there is an increasing order of specific capacitance measured from cyclic voltammogram at 100 mV/s: SnO\(_2\)–V\(_2\)O\(_5\)–CNT composite (121.40 F/g) > SnO\(_2\)–Al\(_2\)O\(_3\) mixed oxide (88.90 F/g) > SnO\(_2\)–Al\(_2\)O\(_3\)–carbon composite (69.30 F/g), revealing that ternary composites could be more superior than binary composites if the optimal compositions were achieved. In recent work, Wang and co-workers have successfully prepared nickel cobalt oxide (NiCo\(_2\)O\(_4\))/SWCNT ternary nanocomposite for electrochemical capacitor applications.\(^{108}\) This novel material not only exhibits a remarkable specific capacitance of 1642 F/g, but also demonstrates an excellent cycling stability of 94.1% retention after 2000 cycles. They concluded that the highly conductive SWCNT and NiCo\(_2\)O\(_4\) have helped to reduce the interfacial resistance of the nanocomposite. However, the authors offer no explanation for the enhanced cycling stability of this ternary composite.

Recently, Yan et al. successfully synthesized a novel MnO\(_2\)/PANI/carbon ternary composite in 1 M H\(_2\)SO\(_4\).\(^{109}\) With the 12% MnO\(_2\) loading, the maximum specific capacitance of 695 F/g and the 88% capacitance retention are achieved after 1000 cycles. This study shows that the protective PANI nanolayer enables MnO\(_2\)/carbon composites to be operated in acidic electrolyte. Similar study on ternary composite of MnO\(_2\)/CNT/poly(3,4-ethylenedioxythiophene)-poly (styrenesulfonate) or PEDOT-PSS by Hou et al. reported that the specific capacitance of the ternary composite reaches 200 F/g with only less than 1% decay in specific capacitance after 1000 cycles.\(^{110}\) They suggested that the good conductive CNTs provide high surface for the deposition of highly porous MnO\(_2\) nanospheres and improve the mechanical stability of the composite. In addition, PEDOT/PSS can act as an effective dispersant and binder for improving the adhesion to the substrate and the connection among MnO\(_2\)/CNTs particles. Similarly, Cheng and co-workers\(^{135}\) (2012) adopted novel approach of fabricating ternary nanocomposites of graphene-MnO\(_2\)-CNTs via direct growth of MnO\(_2\) nanoparticles and CNTs on graphene substrate. CNTs which provide electronic conductivity and mechanical reinforcement in combination with highly electrochemically active MnO\(_2\) nanoparticles and high-surface-area graphene enable the synergetic effects for superior nanocomposite electrodes. These flexible electrodes successfully deliver high specific capacitance of 372 F/g without the need of current collectors and binders.\(^{135}\)

Another research group has reported on a novel PANI/TiO\(_2\)/graphene oxide (GO) composite which demonstrated the highest specific capacitance of 1020 F/g.\(^{111}\) TiO\(_2\) nanoparticles serve as avenue for electrode to penetrate to three-dimensional graphene oxide-PANI networks, facilitating the Faradaic reactions of PANI. To improve its processability, polystyrenesulfonate (PSS) is added and this results in an aqueous dispersion of PEDOT/PSS as PEDOT has good compatibility with polar group polymers. A study on PEDOT/PSS-SWNT composite material has demonstrated that the specific capacitance of 104 F/g is obtained for the 40% SWNT compositions in the polymer matrix.\(^{112}\) Huang et al. have claimed an impressive 1409 F/g for the PEDOT/PSS/RuO\(_2\) composite.\(^{113}\) While
this device shows very promising performance, ruthenium-based starting materials however are too expensive for the large-scale production of commercially viable EC.

Very recently, an electrode of NiCo$_2$O$_4$ mesoporous nanosheets grown on conductive Ni foam is found to be able to demonstrate an excellent electrochemical performance. The highly porous NiCo$_2$O$_4$ nanosheets with increased electroactive sites have greatly facilitated the ionic and electronic transport. Moreover, the new concept of directly grown NiCo$_2$O$_4$ nanosheets on conductive substrate has ensured good electric contact and good mechanical adhesion for high-performance electrodes.$^{136}$ Similarly, another novel design of composite electrodes has been realized by facile coating nanometer-thick redox active MnO$_2$ thin film to highly electronic conductive Zn$_2$SnO$_4$ nanowires which are directly grown on flexible carbon microfibers in 1 M Na$_2$SO$_4$. In such a composite, the maximum specific capacitance of 642 F/g is achieved through the synergetic contributions from MnO$_2$, Zn$_2$SnO$_4$ and carbon microfibers.$^{137}$

Table 1 summarizes the recent research works that were carried out in relation to the symmetric composite electrodes, including different combinations of material, various fabrication/synthesis techniques as well as different electrolytes employed. The highest value of 2223 F/g is reported for CoOPy composite electrode.$^{132}$ This is followed by NiCo$_2$O$_4$/Ni (1743 F/g),$^{136}$ NiCo$_2$O$_4$/CNT (1642 F/g)$^{108}$ and TiO$_2$/PANI/graphene (1020 F/g)$^{111}$ In general, RuO$_2$-based composites such RuO$_2$/SnO$_2$ (690 F/g),$^{47}$ RuO$_2$/TiO$_2$ (640 F/g),$^{72}$ RuO$_2$/NiO (210 F/g)$^{70}$ and RuO$_2$/AC (185 F/g)$^{48}$ are not able to achieve as high as those of pure RuO$_2$-based electrodes, ranging from 720 F/g to 1190 F/g; nevertheless, the overall electrode fabrication cost is greatly reduced. MnO$_2$-based and NiO-based, composites which are most widely investigated after RuO$_2$-based materials, generally demonstrate the capacitance values between 160 F/g to 400 F/g. Cost continues existing as a major challenge to the mass production of EC particularly for high-performance applications. In view of this, the recent development of cost-effective electrode materials is underway by a...
number of researchers. With the synergic effect from novel advanced materials, continual effort is still worth in developing composite electrode, owing to its feasibility, availability and compatibility for future electrochemical capacitor fabrication.

4.3.10. New materials: Lithium metal oxide-based composites and lithium-ion capacitor

A new generation of hybrid capacitor-battery designs utilizing battery-type and electrochemical capacitor-type electrodes are found to obtain higher energy storage than currently available commercial EC. The use of these lithium metal oxides in hybrid capacitor results in excellent cyclability and rate capability, offering alternatives for the lifespan limitations associated with batteries as well as unsatisfactory energy density of capacitors. Amatucci et al. first proposed the Li$_4$Ti$_5$O$_{12}$/AC hybrid energy storage system which is able to achieve more than 10 Wh/kg in acetonitrile solution. Following this work, other systems have been designed, coupling a negative lithiated compound to a positive AC at low voltage. The nonaqueous asymmetric hybrid capacitors utilizing lithium-intercalated compounds (Li$_4$Ti$_5$O$_{12}$) negative electrode and AC positive electrode was introduced by Telcordia Technologies in 2002. These 500 F devices were made in the same technology as Li-ion batteries, demonstrating specific energy of 11 Wh/kg in 2 M LiBF$_4$. Additionally, the cycle-life of this lithiated electrode is more superior as compared to Li-ion batteries, approaching that of EC. Nevertheless, this novel study shows that the internal resistance of the device increases during the course of discharge as a result of the delithiation of the Li$_4$Ti$_5$O$_{12}$ anode and subsequently becomes less conductive. Similarly, Naoi and co-workers have developed another nanohybrid capacitor that consists of a faradaic Li$_4$Ti$_5$O$_{12}$ negative electrode combined with a AC positive electrode in 1 M LiBF$_4$ organic electrolyte. The study demonstrates that this configuration of hybrid electrochemical capacitor exhibits a higher energy density in comparison to that of a conventional (AC/AC) electrochemical capacitor due to its larger working voltage and higher capacitance, as shown in Fig. 12. Very recently, Jung and co-workers have developed a novel high energy density hybrid capacitor consisting carbon-coated Li$_4$Ti$_5$O$_{12}$ (LTO) negative electrode and AC positive electrode in 1 M LiPF$_6$. As seen in Fig. 13, this advanced hybrid capacitor system with the improved electronic conductivity carbon coating on

<table>
<thead>
<tr>
<th>Composite electrode</th>
<th>Configuration</th>
<th>Electrolyte</th>
<th>Specific capacitance (F/g)</th>
<th>Year of publication</th>
<th>Reference</th>
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<td>Fe$_3$O$_4$/MWNT</td>
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<td>MnO$_2$/Zn$_2$SnO$_2$/carbon</td>
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<td>1 M Na$_2$SO$_4$</td>
<td>642</td>
<td>2011</td>
<td>137</td>
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<tr>
<td>Ag/CuO</td>
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<td>6 M KOH</td>
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<td>77</td>
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<td>MnO$_2$/PANI/carbon</td>
<td>Metal oxide/polymer/carbon</td>
<td>1 M H$_2$SO$_4$</td>
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<tr>
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<td>415</td>
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<td>W$<em>{15}$O$</em>{40}$/PANI</td>
<td>Metal oxide/polymer</td>
<td>H$_2$SO$_4$</td>
<td>Smart electrode</td>
<td>2014</td>
<td>134</td>
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</tbody>
</table>

$^a$Measurement using two-electrode cell configuration.
Li$_4$Ti$_5$O$_{12}$ electrodes, offers the maximum specific energy of 35.5 Wh/kg which is higher than that achieved by AC/AC conventional EDLC. In the study, the authors proposed that the Li$^+$ cations are intercalated into the carbon-coated Li$_4$Ti$_5$O$_{12}$ negative electrode whereas the PF$_6^-$ anions are adsorbed onto the high surface area AC positive electrode during charging while both anions and cations are then released during discharging.

Another novel Li-ion capacitor was successfully fabricated using AC as cathode and LiCrTiO$_4$ as anode in 1 M LiPF$_6$, delivering specific capacitance, maximum energy and power densities of 83 F/g, 23 Wh/kg and 4 kW/kg, respectively. Bockenfeld et al. (2011) have developed composite electrodes consisting of 65 wt.% LiFePO$_4$ and 20 wt.% AC in 1 M LiPF$_6$, displaying very high specific capacitance of 140 mAh/g or 504 F/g. By adding 10 wt.% conductive carbon, the electronic conductivity of this composite electrode is increased significantly. However, the 100-cycle test analysis obtained from the study could not convince a good cycling performance for this composite electrode. A novel hybrid capacitor fabricated with LiFeSiO$_2$ and AC in 1 M LiPF$_6$ delivers the specific capacitance of 49 F/g, the specific energy of 43 Wh/kg and the specific power of 200 W/kg. Another study on the novel hybrid capacitor made of Li$_2$MnSiO$_4$ anode and AC cathode has reported the specific capacitance of 43.2 F/g (two-electrode cell) in 1 M LiPF$_6$ with high specific energy of 54 Wh/kg and specific power of 150 W/kg. This hybrid capacitor exhibits good cycleability, retaining about 85% of its initial capacitance after 1000 cycles.

To the best of our knowledge, very few studies aimed at designing lithium metal oxide-based electrode materials using aqueous electrolyte. Wang and Xia have developed the hybrid capacitor consists of AC negative electrode and LiMn$_2$O$_4$ positive electrode in Li$_2$SO$_4$. This new concept aqueous-based hybrid capacitor is different from any other hybrid capacitors or Li-ion batteries which mostly employ nonaqueous electrolytes. In general, the Li$_2$SO$_4$ aqueous electrolyte behaves the same profile as that in EDLCs. It is apparent from Fig. 14 that the AC/LiMn$_2$O$_4$ hybrid capacitor exhibits higher specific energy and power densities compared to the AC/LiMn$_2$O$_4$ hybrid capacitor with higher specific energy and power densities compared to those of AC/AC conventional EDLC in Li$_2$SO$_4$. 

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**Fig. 12.** Comparison of voltage profile for a hybrid lithium-ion capacitor consists of AC cathode and Li$_4$Ti$_5$O$_{12}$ and a AC/AC conventional EDLC.

**Fig. 13.** Ragone plot comparing lithium-ion batteries, carbon-coated Li$_4$Ti$_5$O$_{12}$/AC lithium-ion capacitors and AC/AC conventional EDLCs.

**Fig. 14.** Ragone plot showing AC/LiMn$_2$O$_4$ hybrid capacitor with higher specific energy and power densities compared to those of AC/AC conventional EDLC in Li$_2$SO$_4$. 

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those of AC/AC conventional EDLC. The practical specific energy of the AC/LiMn$_2$O$_4$ can be as high as 14 W h/kg. In other study, the hybrid capacitor consisting of LiMn$_2$O$_4$ working as a positive electrode and AC as negative electrode in 1 M Li$_2$SO$_4$ has proven to be able to deliver a capacity of 60 F/g with high specific energy of 36 Wh/kg in two-electrode cell.$^{124}$

Very recently, Naoi’s group has identified that the conventional lithium metal oxides have the greatest drawback of low power characteristics as a result of poor Li$^{+}$ diffusion coefficient and poor electronic conductivity.$^{67}$ To overcome these problems, further development on composite electrode materials which couple lithium metal oxide powder with other electroconductive material may become a versatile solution. With regards to this, the research group has developed lithium-ion capacitors comprise AC cathode and conductive graphite/AC anode pre-doped with lithium ions. It is suggested that the adsorption–desorption of anions from electrolytes occurs on the AC electrode while lithium intercalation–deintercalation occurs in the graphite electrode.$^{67}$ Similarly, Sivakkumar and Pandolfo have fabricated a lithium-ion capacitor assembled with pre-lithiated graphite anode and AC cathode, exhibiting energy density of 100 Wh/kg.$^{125}$ However, the study reveals that the instability of pre-doped graphite during the cycling is the main root cause of the capacity deterioration. The work is still in its preliminary stage and much research is needed before this novel lithium-ion capacitor can be realized as potential charge storage device which is complementary to lithium-ion batteries.

5. Conclusions

In summary, the electrode material of electrochemical capacitor needs to satisfy three basic requirements: (1) high capacitance, (2) low resistance and (3) good cycling performance. To widen their applications in the new technologies associated with energy conversion and storage, the enhancement in capacitance and energy density is urgently demanded. Consequently, it is very likely that continual research efforts will be aimed to discover new electrode materials with high performance and low cost. Future trends of electrochemical capacitor are devoted to the pseudocapacitive materials, especially metal oxides and their composites with carbonaceous materials, which store charges through fast and reversible faradaic reactions. Carbon-based materials such as AC, CB, CNTs and graphene have been utilized to support various metal oxides or conducting polymers for making composite electrode materials. While carbonaceous materials offer the advantage of excellent electrical conductivity, the observed enhancement of electrochemical performance becomes more pronounced when only a small amount of metal oxide is loaded on the electrode. However, for practical applications such as hybrid electric vehicle (HEV), high mass loading of total active materials with metal oxides are highly demanded. Conversely, when the loading of metal oxides is too high, metal oxide particles become agglomerated with dense morphology and limited accessible surface area. As a result, these lead to high resistance and a comparatively low specific capacitance which eventually hinder the electrode materials from future applications in electrochemical capacitor. Therefore, the low-energy density caused by the limited loading of cost-effective metal oxides still remains a major problem. Extensive efforts are still needed to improve the electrochemical utilization of these metal oxides, especially in the cases where high metal oxide loading is needed. Regarding these limitations, composite electrodes fabricated from different configurations including binary and ternary composites have been attempted. Another possible hybrid cell configuration is the combination of lithium metal oxide electrode with the other capacitive nonFaradaic electrode with the purpose of producing higher operating voltage and capacitance. Combination of EDLCs, pseudocapacitors with the latest generation of lithium metal oxide has brought the energy density of EC closer to that of batteries. However, the limited charging rate owing to low Li$^{+}$ diffusion coefficient and poor electronic conductivity would be the possible drawback of the lithium metal oxide electrodes. Overall, the key to achieving high-performance energy storage systems is to explore novel electrode material systems coupling nanostructured materials with rational design combination that offer excellent electronic conductivity and cyclic stability.

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