

New Materials and New Configurations for Advanced Electrochemical Capacitors

by Katsuhiko Naoi and Patrice Simon

Today, electrochemical capacitors (ECs) have the potential to emerge as a promising energy storage technology. The weakness of EC systems is certainly the limited energy density, which restricts applications to power delivery over only few seconds. As a consequence, many research efforts are focused on designing new materials to improve energy and power densities. These are reviewed below.

Challenges for Higher Energy Density

Since the energy density is a product of capacitance and squared voltage (or voltage), strategies aimed at increasing both of them are of particular importance (Fig. 1). An electrochemical double-layer capacitor (EDLC) stores electrical charge in an electrical double layer at the electrode-electrolyte interface. High surface area electrode materials, such as activated carbons, maximize this interface, resulting in larger capacitance. More recently, new categories of carbon materials have been proposed with much higher surface area: carbon nanotubes (CNTs) or fibers (CNFs) and fine-tuned microporous carbons, which still rely on reversible ion adsorption as the charge-storage mechanism.^{1,2} These carbon materials are made by fine pore-size control and dimensional control, which enables optimized ionic diffusion and high capacitance.

Ruthenium Oxides and Pseudocapacitor Materials

In addition to high-surface-area carbons, even higher capacitance can be achieved by using redox-active materials such as metal oxides³⁻⁶ and conducting polymers^{7,8} (Fig. 2). These materials store electrochemical charge using highly reversible surface redox reactions, commonly described as “pseudocapacitance” in the literature. The introduction of these fast, reversible surface processes has drastically increased the charge-storage performance. As mentioned before, electronically conducting polymers (ECPs) are well known as pseudocapacitive materials.⁹ Many studies have been done on the synthesis and characterization of ECPs for applications in batteries and ECs. High pseudocapacitances have been achieved and reported mainly with

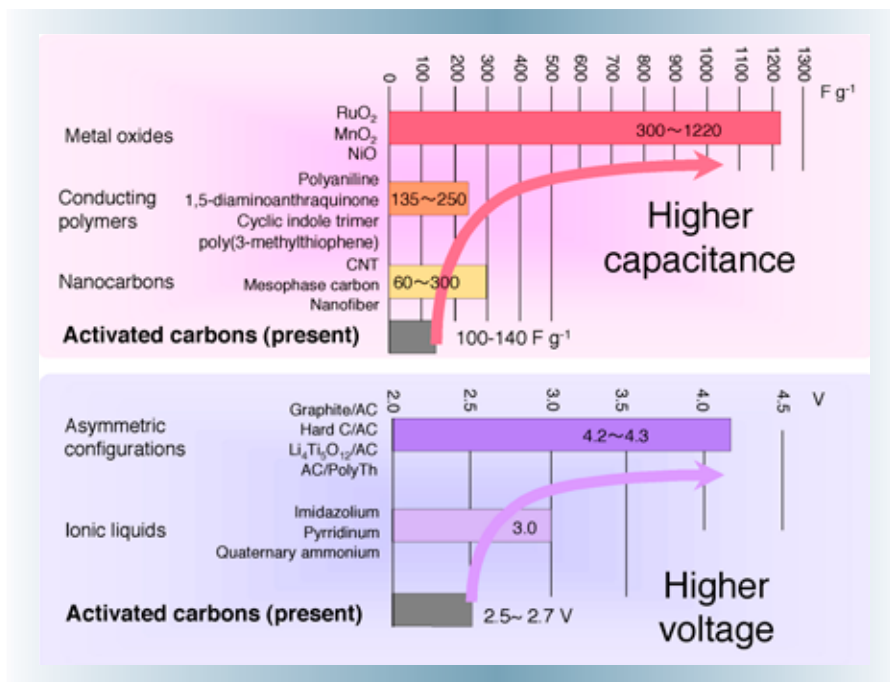


Fig. 1. Challenges for higher energy density for ECs.

thiophene-based polymers. Cell voltage can be high when using n- and p-doped polymers respectively at the negative and positive electrode. However, as discussed elsewhere in this issue, the cycling behavior of these systems is still uncertain.

Hydrous ruthenium oxides ($\text{RuO}_2 \cdot 0.5\text{H}_2\text{O}$)^{1,2} have been intensively studied for pseudocapacitors because of their high theoretical specific capacitance (1358 F g⁻¹) and high electrical conductivity ($3 \times 10^2 \Omega^{-1} \text{cm}^{-1}$). In 1995, Jow, Zheng, *et al.* reported

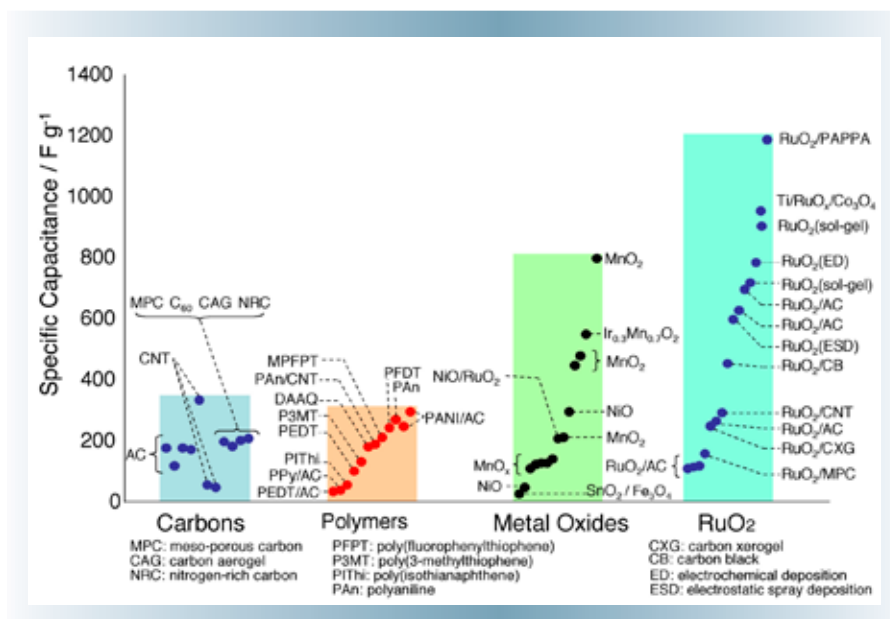


Fig. 2. Proposed pseudocapacitor materials in the literature.

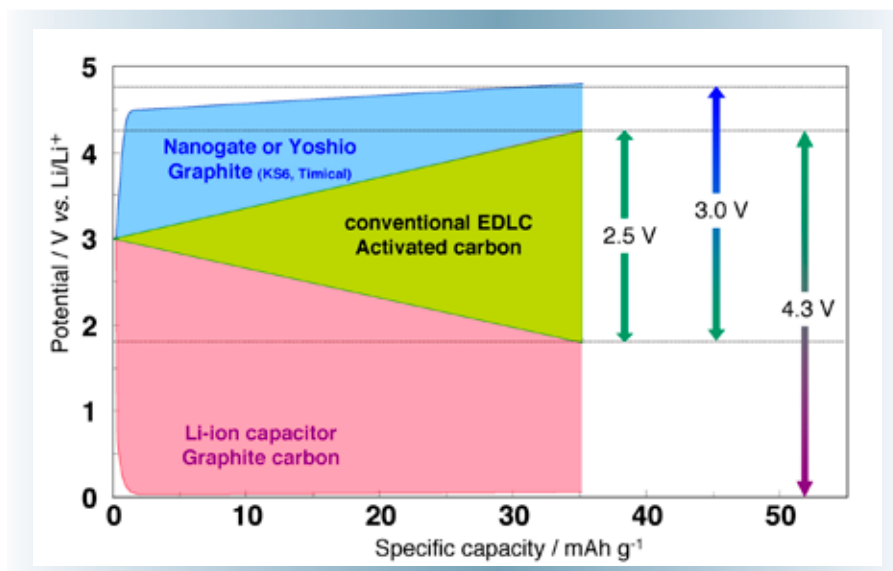


FIG. 3. Asymmetric ECs with different carbon anodes and cathodes.

amorphous hydrous RuO_2 prepared by sol-gel methods that exhibited a specific capacitance of 720 F g^{-1} .^{3,4} Such a high capacitance is attributed to hydrous surface layers that enable facile transport of electrons and protons.¹⁰ However, the capacitance decreased rapidly at higher rates due to proton depletion and over-saturation in the electrolyte during charge-discharge cycling.¹⁰ A two-dimensionally controlled RuO_2 nano-sheet was fabricated by Takasu, Sugimoto, *et al.*¹¹ for better electron-proton transport. In order to improve the rate performance, many researchers have attempted to combine small particles of hydrous RuO_2 with carbon materials, such as with activated carbons,¹²⁻¹⁵ carbon black (CB),¹⁶ and CNTs.¹⁷ Such composites certainly improve the rate capability of hydrous RuO_2 . For instance, Hu, *et al.*¹⁵ prepared nano-sized (3 nm) hydrous RuO_2 /carbon composites exhibiting specific capacitance of $850\text{-}1200 \text{ F g}^{-1}$ (per RuO_2) at low (10 to 20 wt %) loading of RuO_2 . However, as the RuO_2 content increases, the specific capacitance gradually decreases due to low utilization by particle aggregation. Accordingly, the specific capacitance per composite decreased with RuO_2 content and was only 288 F g^{-1} even at 50 wt. % of RuO_2 . It is necessary to achieve not only higher specific capacitance per RuO_2 but per total mass of the composite materials. Very recently, Naoi, *et al.* reported that a super-highly dispersed nano-sized (0.5 to 2 nm) hydrous RuO_2 /KB composite could be prepared by *in situ* sol-gel process induced by ultra-centrifugal mechanical agitation.¹⁸ After annealing at 150°C , the composite shows a high specific capacitance of 821 F g^{-1} (per composite). ECs based on RuO_2 and other oxides including MnO_2 and NiO are better configured in aqueous media and some of them are being investigated for miniaturized devices because of their cost effectiveness.

Nano-architected Electrodes for Pseudocapacitors

There have been approaches to build nanostructured architectures with pseudocapacitive materials by themselves. Good examples have been demonstrated by the AIST group for fabricating TiO_2 , $\text{TiO}_2\text{-P}_2\text{O}_5$ template electrodes that allow 1D or 2D ion transport.¹⁹ Nano-decoration has been attempted on high surface area CNTs with mono or nanolayers of many types of pseudocapacitive materials. Thus MnO_2 ,²⁰ ECPs,^{21,22} and TEMPO²³ have been coated onto CNTs to maximize the charge efficiency and power capability. The fine-tuning of the nanoscale-decoration of these electrode materials will ultimately result in optimal performance in terms of energy and power capabilities as well as cyclability.

Hybrid EC Devices

Dramatic enhancements in energy storage can be made by use of asymmetric combinations of different cathodes and anodes, producing a higher working voltage. An example is the combination of an EDLC electrode with a battery-like one, the latter possibly being pseudocapacitive. In such systems, called "asymmetric hybrid capacitors," the battery-like electrode provides high energy density while the EDLC electrode enables high power capability in the system. By designing electrolytes for optimum performance in such asymmetric configurations, the critical need for high-voltage operation may be achieved without compromising stability or long-term cyclability.

There are also studies on ionic liquids and new types of electrolyte systems for batteries and possibly for ECs.²⁴ However, in this article, the authors focus on common non-aqueous media, such as carbonate-based electrolytes. As

shown in Fig. 3, one type of hybrid system has been developed based on EDLC technology. A negative EDLC carbon electrode is combined with a positive graphite electrode where the anion insertion (partly with electrolyte intrusion) reaction occurs at over 4 V vs. Li/Li^+ .²⁵ Such new carbon materials, for example, "nanogate-carbon,"²⁶ exhibit higher specific energy and capacitance (140 F cm^{-3}). However, a volume expansion (20-200%) was reported after cycling,²⁷ which may lead to disintegration²⁸ of the capacitor cell due to intrusion of electrolytes. Before going further into details, it should be noted that in such systems energy density improvements are usually achieved by partially sacrificing long-term cycle life. However, if some applications can compromise cycle life, the hybrid systems offer a very promising solution for improved energy density.

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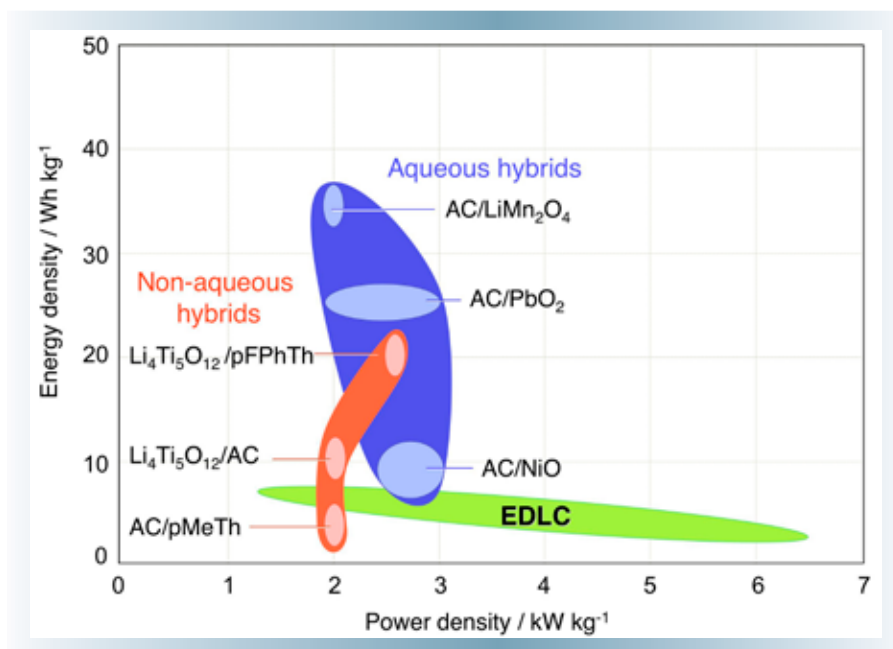


Fig. 4. Various proposed asymmetric ECs.

There are many other pseudo-capacitive materials that can be used to assemble higher performance ECs. Recently, various configurations have been suggested for asymmetric hybrid capacitors (Fig. 4).

One of the first hybrid systems developed combined activated carbon (AC) with $\text{Ni}(\text{OH})_2$ in an aqueous KOH electrolyte, presenting very high power performances at very low temperatures (-20°C), ideal as a device for cold cranking in extreme conditions, including military applications.²⁹ Another approach has been proposed, also using aqueous electrolytes, assembling a negative EDLC electrode on a positive lead-acid battery electrode (AC / PbO_2). High cell voltage (2.1 V), high power density (as compared with lead-acid battery), and lower cost make this system promising for applications where power is needed. AC/ MnO_2 systems also operating in aqueous electrolytes have a high cell voltage (2 V) and high capacitance. Another feature article in this special issue is devoted to this system.

Hybrid systems combining a carbon EDLC negative electrode with a positive ECP one have garnered much interest in recent years. Polythiophene and its derivatives have shown to exhibit high capacitance, especially polymethylthiophene (pMeT).⁹ A cell voltage of 3 V in a PC-based electrolyte could be reached, while still maintaining the high capacitance value for the pMeT component.⁹ However, long-term cyclability was compromised to some extent by the electrolyte voltage window. In this regard, the ECP electrochemistry in ionic liquids

has been studied by Mastragostino, *et al.* and Paserini, *et al.* and promising results have been obtained.²⁴

Lithium Ion Hybrid Capacitors

The worldwide intensive research on Li-ion batteries developed in the past few years has also boosted the research on hybrid EC systems in non-aqueous electrolytes. Various systems have appeared in the literature combining a Li-intercalation anode and a positive AC electrode. The $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{acetonitrile}/\text{AC}$ system first proposed by Amattucci, *et al.* was one of the first to achieve more than 10 Wh kg^{-1} (at 3.2 V) with good power capability.^{30,31} Following this work, other systems have been designed, coupling a positive AC to a Li-intercalation anode operating at low voltage.³² Fuji Heavy Industry announced a hybrid capacitor using a pre-lithiated (pre-doped with lithium ions) AC or polyacene as the negative electrode and an AC as the positive one. Devices with cell voltages as high as 3.8 V have been achieved with energy density up to 25 Wh kg^{-1} . The Li pre-doping is a key technology that shows that: (1) high voltage ($\sim 4 \text{ V}$) can be achieved without excess charging, (2) irreversible capacity of the negative electrode can be suppressed, (3) electrode resistance is lowered, and (4) cost performance is higher than EDLCs. Volumetric energy density has been reported as high as 30 WhL^{-1} . For commercialization, further development is needed to avoid solid electrolyte interface accumulation on negative electrodes for safety and better cycling characteristics.

Outlook

Revolutionary concepts for the design of electrodes, electrolytes, and interfaces have been suggested. For instance, the integration of multiple physico-chemical functionalities or the synthesis of materials with fine-tuned micro- and mesopore size distributions show enhanced charge-storage efficiency. Also the search for new materials and nanofabrication technology has enabled the development of nano-architected electrodes for high performance pseudocapacitors as well as hybrid devices with appropriate dimensional control for ion channels. The continuing improvements in the material properties and electrode designs as well as the development of different hybrid strategies bode well for increasing the energy and power densities in ECs. ■

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