Advanced Polymers as Active Materials and Electrochemical Capacitors and Hybrid Capacitor Systems

Advanced Polymers as Active Materials and Electrolytes for Electrochemical Capacitors and Hybrid Capacitor Systems

by Katsuhiko Naoi and Masayuki Morita

Recent advancements in nanotechnology have resulted in the development of new materials and a greater fundamental understanding of their properties. Those advancements are currently being applied to revolutionary designs of ECs and are enabling new types of hybrid energy-storage devices that exhibit characteristics of batteries and ECs. Some of these new designs utilize polymer electrodes or polymer electrolytes and some unique combinations as cell components are proposed. In this article, the authors will describe the recent advancement in polymer electrodes and electrolytes investigated for use in advanced ECs.

Polymers as Electrode Materials in Electrochemical Capacitors

Asymmetric ECs, often called pseudocapacitors or hybrid electro-chemical capacitors, can be configured with redox-active polymer electrodes. Redox polymers can provide higher capacitance and/or higher power capability than activated carbon electrodes utilized in conventional electrochemical double layer capacitors (EDLC)s.

Figure 1 shows π-conjugated conducting oligomers and polymers with various heterocyclic organic compounds as well as other organic redox molecules in the order of their theoretical capacity (in Ah kg^{-1}). These organic electrodes can be charged and discharged at relatively higher rates than activated carbon electrodes in EDLCs, providing high power, high chemical stability, high capacity, and long-term cyclability. In addition, to achieve high power and energy density, the organic electrodes are expected to enable the following properties through their molecular design: (i) devices of various and flexible shapes, (ii) light-weight devices due to their low specific gravity (1.0-1.2), and (iii) potential bio-degradability (environmentally friendly because no heavy metals are required).

Organic Materials for ECs.—As shown in Scheme 1, there are many organic materials for ECs. These organic molecules can be operated in nonaque-ous or aqueous electrolytes (e.g., sulfuric acid solution). It has been reported that poly-3-methylthiophene (b),[1] poly-fluorophenylthiophene (e),[2] and polyaniline (h)[3] can be operated in nonaqueous electrolytes, such
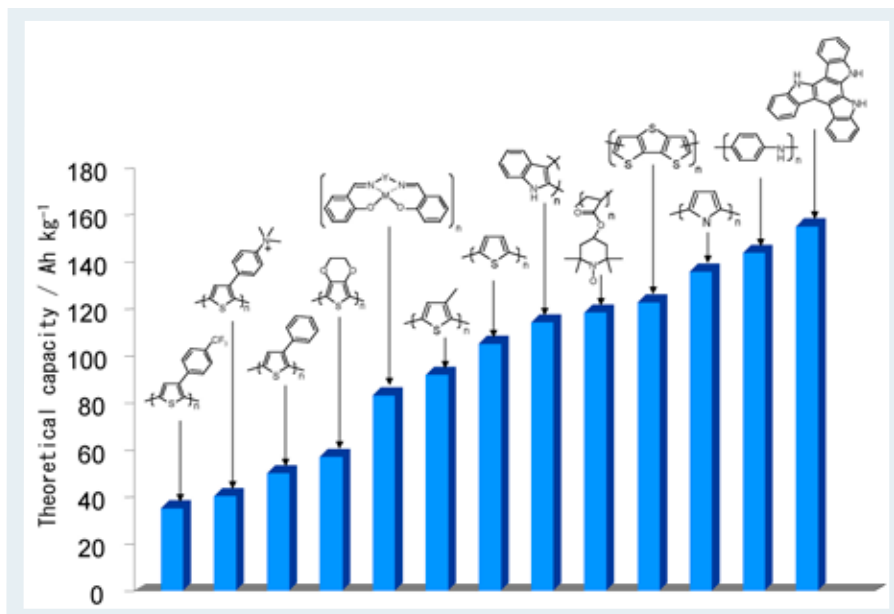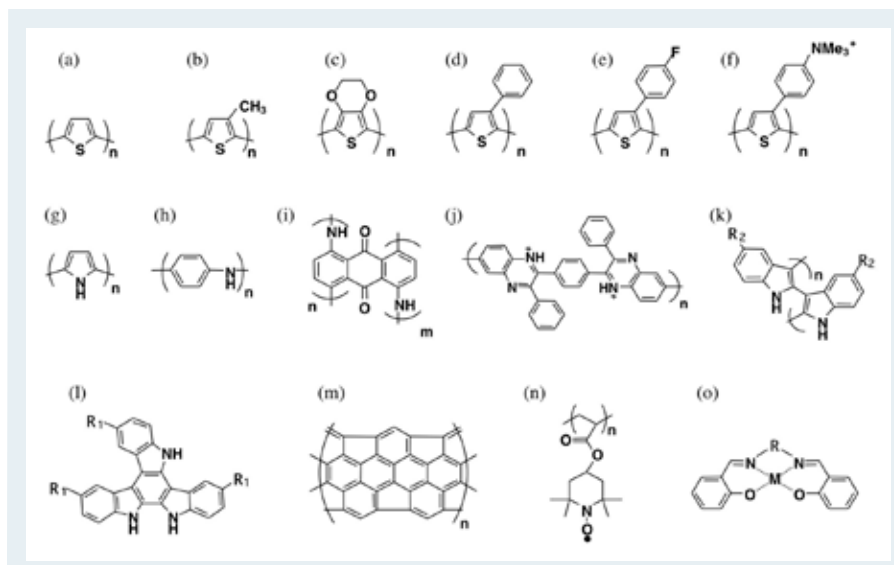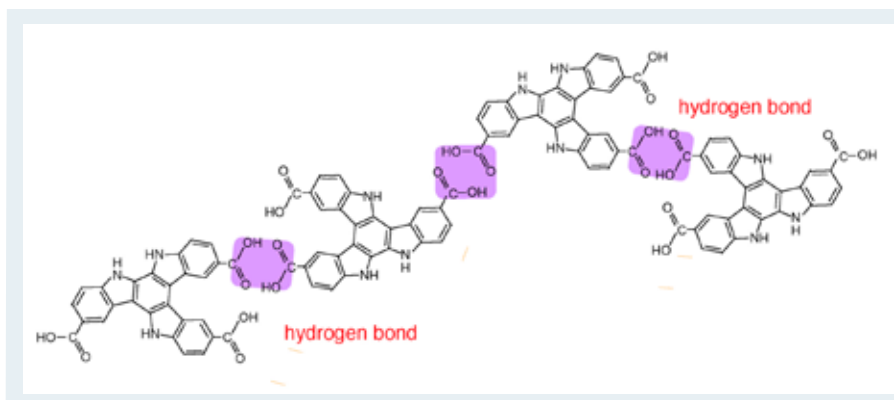

FIG. 1. *Various polymers or organic materials studied for ECs and polymer batteries.*

as Et_4NBF_4 solutions in propylene carbonate. Among those, poly-1,5-diaminoanthraquinone (i)[4,5] showed a high specific capacitance of 200 - 300 F g^{-1} but only in an acidic aqueous electrolyte. Normally when conducting polymers are cycled repeatedly, degradation occurs and the capacity fades. A good cyclability (>50,000 cycles) was shown for the cyclic indole trimer[l] and the network of carboxyCIT supramolecules (Scheme 2) as the most cyclable organic based ECs.[6,7] This was achieved by having a cyclic conformation in which 2- and 3-positions are close to one another in order to avoid over-oxidation and hydrolysis.
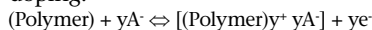

SCHEME 1. *Organic materials for ECs include: polythiophene and its derivatives (a)-(f), polypyrrole (g), polyaniline (h), poly-1,5-diaminoanthraquinone (i), polyquinoxaline (j), polyindole (k), cyclic indole trimer (l), polyacene (m), tetramethylpyridine derivatives (stabilized radical) (n), and metal complex polymer (o).*
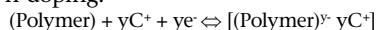
Scheme 2. *A network structure of carboxyCIT molecules via hydrogen bonding.*

Electric energy can be stored and delivered in conducting polymers as delocalized π-electrons are accepted and released during electrochemical doping/undoping, respectively. There are two types of doping process below:

p-doping:
$$(Polymer) + yA^- \Leftrightarrow [(Polymer)^{y+} \, yA^-] + ye^-$$

n-doping:
$$(Polymer) + yC^+ + ye^- \Leftrightarrow [(Polymer)^{y-} \, yC^+]$$

Conducting polymer ECs were classified into three types.[13] Type I capacitors utilize p-doping conducting polymers, such as polypyrrole, polythiophene, and polyaniline, for both positive and negative electrodes (Fig. 2a). The type I capacitors show low operating potential (< 1 V), and only half of the total capacity (Q_I) can be utilized. Type II capacitors have an asymmetric configuration that utilize p-doping and n-doping polymers as positive and negative electrodes, respectively. The proton polymer battery is the one practical
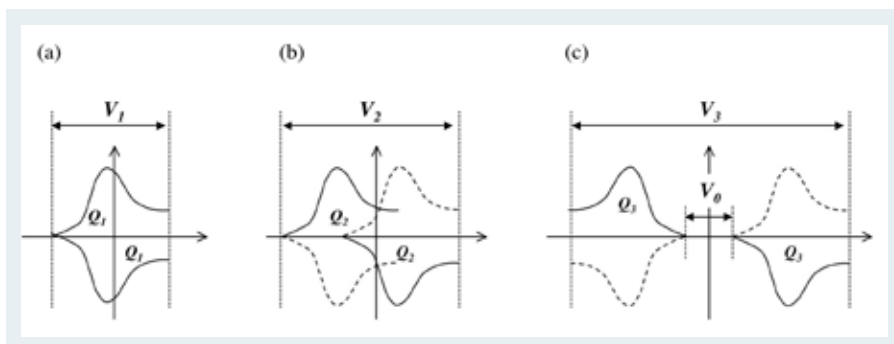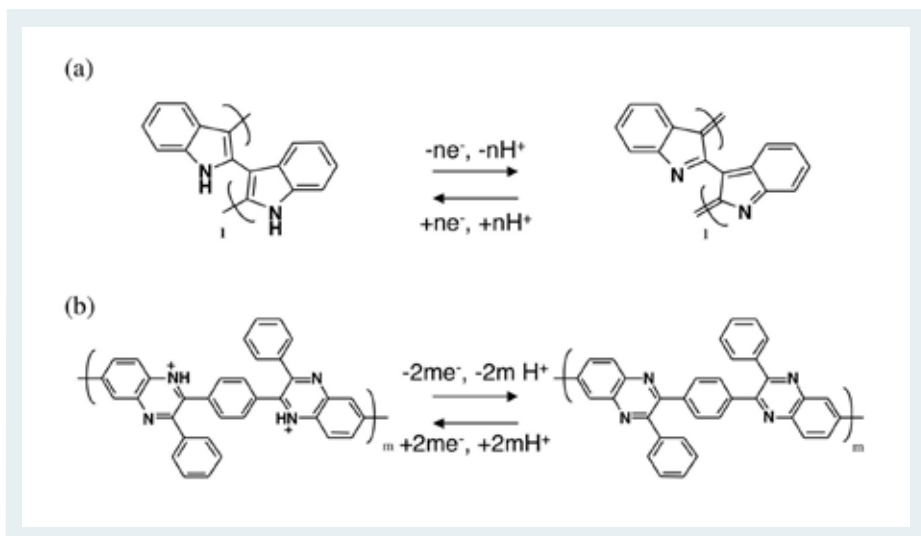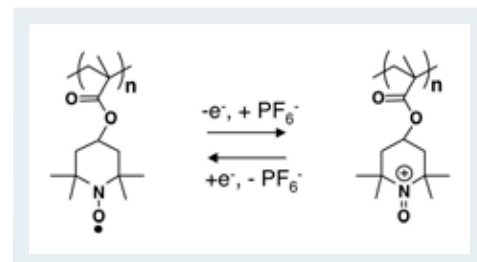
application of this type. The type II capacitors provide higher capacity (Q_2) and higher working voltage than type I capacitors (Fig. 2b). Type III device utilizes the same n- and p-doping conducting polymers such as polythiophene derivatives[9,10] and polyacene,[11] for both positive and negative electrodes. Type III capacitors can provide the widest operating voltage (2.5-3.0 V), about two times higher than type II (Fig. 2c), and the highest energy density can be obtained among three of the types. The type III capacitors have similar discharge characteristics to batteries, where operating voltage drops very rapidly after discharge.

Proton Polymer Batteries.—In 1999, NEC-TOKIN developed a new energy-storage device called "proton polymer battery," which utilizes two kinds of proton-exchanging conducting polymers for positive and negative electrodes. It has the following unique characteristics: (i) fast charge/discharge, similar to ECs, (ii) is maintenance free, and (iii) is durable at low temperatures at -20°C. The working voltage is about 1.2 V when polyindole derivatives are used as positive electrodes.[12] As a negative electrode material, polymers of quionoxaline derivatives can be used.[13]

Proton polymer batteries (see Scheme 3) made of polyindole positive electrode and polyquinosaline negative electrodes can be operated at 1.2 V, with energy density of 5-10 Wh kg^{-1} and power density of 1 kW kg^{-1}. Unlike other battery systems, these energy devices can be charged fast like ECs.

ECs with Stabilized Organic Radical Electrodes.—NEC Corporation has developed a new electric energy storage device, using a stabilized organic radical as the positive electrode.[14,15] Normally, organic radicals are too unstable to degrade readily via hydrogen elimination. When hydrogen atoms are replaced by protective substituents such as those from the methyl group, deterioration and degradation can be prohibited, providing stabilized radicals.

For instance, in 2,2,6,6-tetramethylpiperidinyloxy methacrylate (PTMA; shown in Scheme 4), the polymers of stabilized tetramethylpiperidinyloxy (TEMPO) radical, undergo a reversible redox reaction in organic electrolyte. The energy density and power density of the PTMA capacitors were 20-30 Wh kg^{-1} and 10 kW kg^{-1}, respectively.

Fig. 2. *Classification of ECs utilizing conducting polymers.*

Scheme 3. *Proton polymer battery: (a) polyindole cathode and (b) polyquinoxaline anode.*

Scheme 4. *Fast redox process in PTMA.*

ECs with Metal Complex Polymer Electrodes.

—Nippon Chemi-Con developed a new-type capacitor, "ASED," which utilizes a metal complex polymer (structure (o) in Scheme 1), developed by GEN3 PARTNERS, for the negative electrode and activated carbon for the positive electrode. Energy density was about 20 Wh L^{-1}, maintaining high power density comparable to EDLCs. The advantages are: (i) no degradation at high temperature up to 60°C, (ii) excellent cyclability (>100,000 cycles), (iii) higher operating voltage (3.0 - 3.3 V) than EDLCs, (iv) low cost, and (v) various cell shapes with high flexibility of polymer electrodes.

Polymers as Electrolyte Materials for ECs

Utilization of a solid ion-conductor as the electrolyte component has been attempted in order to fabricate an all-solid EC device, similar to rechargeable battery systems. The merits of the solidification of the electrolyte in such energy devices would be to avoid the risk of electrolyte leakage from the cell that would cause various problems on the system reliability and safety. A solid-state EDLC using polymeric electrolyte was first reported by Yamamoto, *et al.*[16] in early '90s. They observed high specific capacitance under a limited charge-discharge cycling condition. However, further improvements in the system were required to obtain practical capacitor performances. In designing such all-solid electrochemical devices and in order to maintain the contact between solid electrode and solid electrolyte phases, a kind of "flexible interface" is needed, where the fast charge (or ion) transfer process can occur. The ionic mobility in the solid phase is generally too low to be used in capacitor devices at ambient temperature. From these standpoints, a concept of polymeric gel electrolyte (PGE) has been introduced and examined extensively, especially for the EC system.

Solid Electrolytes Consisting of Polymers.

—Because high power density is the strong point of EC device characteristics, high ionic conductivity is a necessary property for electrolytes in ECs. There are some varieties of solid electrolytes based on polymeric materials that have so far been proposed for ECs. For convenience, polymeric electrolytes can be classified into two types, aqueous and nonaqueous (organic) (Table I).
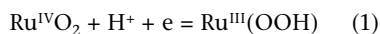
Ionomers, or polyelectrolytes, also called "solid polymer electrolytes (SPEs)," which are well known as the

Table I. Classification of polymer-based solid (gel) electrolytes for EC use.	
Aqueous polymer gel	Ionomer (Polyelectrolyte) (A1) Hydrogel (A2)
Organic polymer gel (non-aqueous)	Alkylammonium-salt in polymer (O1) Acid in polymer (O2)

solid electrolytes in fuel cell systems, are the first candidate of the aqueous solid electrolyte that can be used in ECs. The other type of the aqueous polymeric electrolyte is a complex (or composite) system of a neutral polymeric matrix swollen with an aqueous acidic (or alkaline) solution, which is also called "hydrogel." The former is generally a single-ion (cation or anion) conductor, whereas the latter in principle conducts both cation and anion in the system.

Among the ionomers (Category A1), Nafion®, a typical perfluoro-alkylsulfonate-based ionomer, has been examined in the EC system. Stati and co-workers[17] demonstrated that Nafion® can be utilized in EDLC systems consisting of activated carbon electrodes. They reported as high capacitance with a recast Nafion® electrolyte as with a conventional aqueous acid electrolyte. The better structure would be fabricated for the electrode/electrolyte interface by the recast process of the ionomer. Such electrochemically active materials, as transition-metal oxides and electro-conducting polymers, have widely been examined as electrodes that have high pseudocapacitance. For those electrode materials, organic ionomers can also work as a quasi-solid electrolyte. The above research group[18] reported that the RuO$_2$-based electrode showed high pseudocapacitance with an ionomer/fluororesin composite as the solid electrolyte. The pseudocapacitance of RuO$_2$ is considered to come from the following redox reaction at high surface area.

$$Ru^{IV}O_2 + H^+ + e = Ru^{III}(OOH) \quad (1)$$

That is, the process needs active H$^+$ to give high pseudocapacitance. As acidic ionomers like the Nafion® family provide high H$^+$ activity under hydrous conditions, they would be suitable for the electrolytes of pseudocapacitors using transition-metal oxide electrodes.

The use of second type polymeric composite (Category A2 in Table I) has been demonstrated by Iwakura and co-workers.[19] Typically poly(acrylic acid) (PAA) is swollen with a large amount of aqueous solution to form a physically cross-linked gel that works as PGE for EDLC, as well as an asymmetric capacitor using transition-metal oxide.[20] The basic behavior of the activated carbon or metal oxide electrode in this type of hydrogel is almost the same as in an aqueous electrolyte solution, because the system contains an excess amount of water. However, the hydrogel seems to have the merit of preventing the cell from dry-out of the electrolyte component during long term storage.

Nonaqueous Polymeric Gels.

—Polymeric gels without aqueous components, or nonaqueous gels (Category O1 and O2 in Table I), have also been examined as the electrolytes of EDLC. They consist of either plasticized polymer complexes with electrolytic salts or polar polymer matrices swollen with organic electrolyte solutions. There have been many combinations of polymer-salt-liquid systems so far proposed as the gel electrolytes of ECs. A research group at Yamaguchi University[21] has first reported an all-solid EDLC system using a polymeric gel electrolyte composed of poly(ethylene oxide)-modified polymethacrylate (PEO-PMA) swollen with propylene carbonate that dissolves tetraethylammonium tetrafluoroborate (TEABF$_4$) as the ionic charge carrier. They have also proposed the utilization of poly(acrylonitrile) (PAN)[22] and poly(vinylidene fluoride) (PVdF)[23] as the polymer matrices of PGEs in EDLC. Copolymers of PVdF with hexafluoropropylene (PVdF-HFP) have been used as excellent polymer matrices of gel electrolytes containing alkylammonium salts for EDLC.[24]

Generally in PGE systems, the polymer components serve as the matrix that dissolves the electrolytic salt, dissociates them to their ionic species, and keeps the resulting phase in a solid (gelled) state. With respect to the electrolytic salt in PGE, alkylammonium salts have been used widely for EDLC devices because of their high solubility in such organic solvents as propylene carbonate and high ionic conductivity of the resulting gel electrolyte. Effects of the ions in PGE on the capacitor performances of EDLC are significant. For example, higher specific capacitance is observed for activated carbon electrode in the gel containing trimethylethyammonium (TEMA) salt than that in the gel dissolving tetraethylammonium (TEA) salt.[23] It is worthy of note that higher specific capacitance is often observed in PGE than in the original liquid electrolyte consisting of the same electrolytic salt.[19,23] That is, the polymeric component itself can enhance the electric double layer capacitance of the high surface area carbon electrode. Although the mechanisms of such capacitance
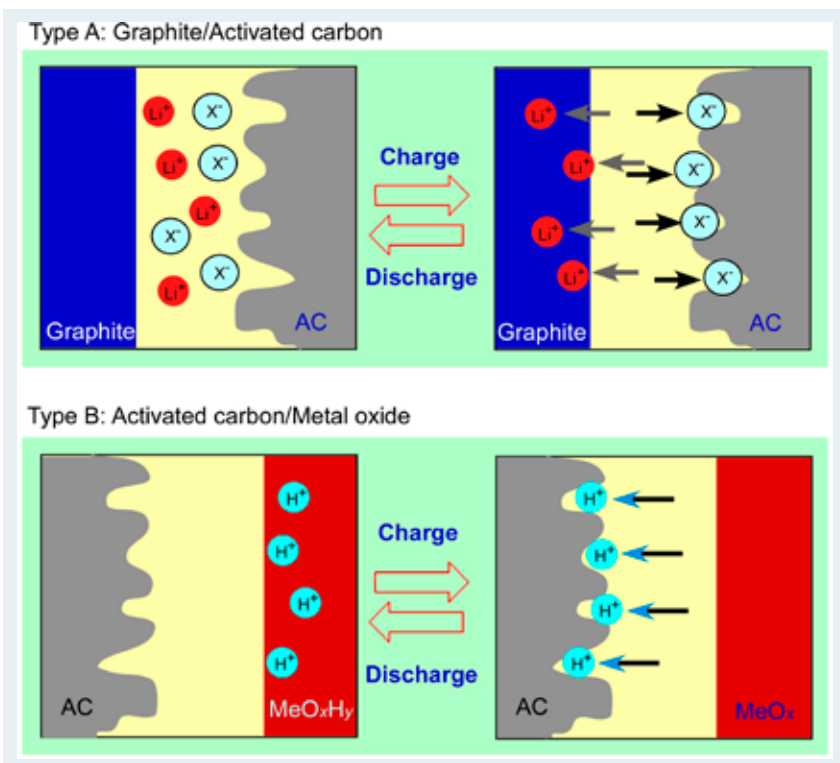
FIG. 3. *Two types of asymmetric ECs using polymeric gel electrolytes. Type A: Graphite/activated carbon with Li+ conducting electrolyte. Type B: Activated carbon/metal oxide with H+ conducting electrolyte.*

enhancements are still unknown in detail, some pseudocapacitance[19] or changes in the double-layer structure[25] can possibly contribute to the additional capacitance in PEGs.

Proton-conducting Nonaqueous Gels.—There are some advantages in using proton conductors for asymmetric ECs that are composed of faradaic and non-faradaic processes at positive and negative electrodes. In Fig. 3, two types of asymmetric EC are schematically shown, in which different types of charge carriers (ions) are needed.

To the rate capability of the capacitor device, proton as the charge carrier will be preferable because of the higher mobility in PGE than that of Li+. A series of acid-polymer-solvent systems have been proposed as the solid-gel proton conductors.[26] They consisted of H_3PO_4 dissolved in poly(methylmethacrylate) plasticized with dimethyl-formamide (PMMA/DMF), or poly(glycidyl-methacrylate) with DMF or propylene carbonate (PGMA/DMF, PGMA/PC).[26,27]

The ionic (proton) conductivity was 10^{-5} to 10^{-4} S cm^{-1} at room temperature, which is lower than that of a hydrogel containing a large amount of water. However, the nonaqueous system is much superior to aqueous hydrogel with respect to the width of the potential window that is closely related to the working voltage of the resulting device. In most nonaqueous PGEs a Grotthus-like mechanism is proposed for the proton conduction.[27] The basic sites of the polymer matrix and/or the plasticizing solvent molecule would act as the proton-receptors, which promotes the fast proton transport even under such anhydrous conditions (Fig. 4).
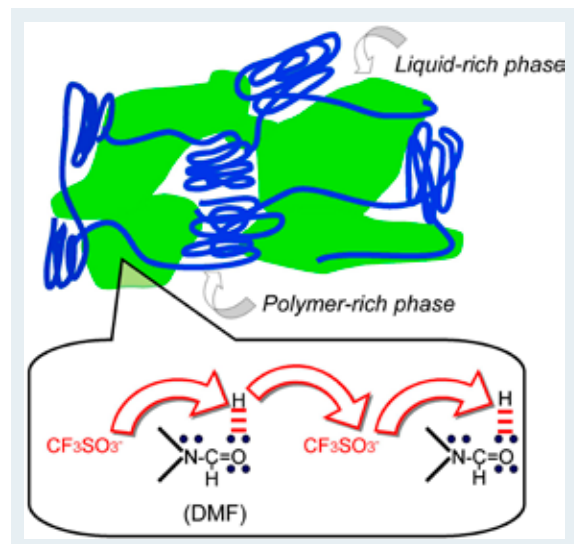
The applicability of the proton-conducting nonaqueous gel as the electrolyte for ECs has been reported.[28,29] An EDLC prototype was fabricated using a nonaqueous gel electrolyte based on PEO-PMA swollen with a poly(ethylene glycol) dimethyl ether (PEGDE) solution dissolving H_3PO_4. It showed as high specific capacitance as that using aqueous acid electrolyte solution at elevated temperature (90°C), despite the lower ionic conductivity relative to the aqueous system.[30] A polymeric gel made of PVdF-HFP swollen with DMF dissolving CF_3SO_3H as the proton source was examined for an asymmetric cell that had activated carbon (AC) as the negative and hydrous RuO_2 as the positive electrode.[29,30] This type of PGE had higher proton conductivity (10^{-3} S cm^{-1}) than the PEO-PMA-based one at ambient temperature, and showed good thermal stability. The asymmetric cell (AC/RuO_2) using the PVdF-HFP-based PGE revealed high specific capacitance, above 300 F g^{-1}-RuO_2, at 60°C. As the system contains no free-water, the operating voltage of the asymmetric AC/RuO_2 capacitor was maximized to 1.6 V or higher.[30] The experimental results suggest that the polymer-based gel electrolytes will be utilized in practical EC systems, especially for high temperature uses.

Outlook

The energy and power capabilities of ECs have been incrementally increased in the past several years. New concepts for capacitive energy storage processes and new functional materials have been proposed. In recent years, there has been renewed interest in electronically conducting polymers and new polymeric electrolytes for high energy ECs and high power batteries. It should be noted here that these approaches have been strongly influenced by the battery and electrocatalysis research communities. Continuing studies and developments of the polymer electrodes and polymer electrolytes will be made in the future for higher performance EC devices as well as high power batteries. ■

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FIG. 4. *Schematic image of H+ conduction in nonaqueous polymeric gel based on PVdF-HFP plasticized with DMF.*

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