



Effect of NaI/I₂ mediators on properties of PEO/LiAlO₂ based all-solid-state supercapacitors

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ABSTRACT

NaI/I₂ mediators and activated carbon were added into poly(ethylene oxide) (PEO)/lithium aluminate (LiAlO₂) electrolyte to fabricate composite electrodes. All solid-state supercapacitors were fabricated using the as prepared composite electrodes and a Nafion 117 membrane as a separator. Cyclic voltammetry, electrochemical impedance spectroscopy, and galvanostatic charge/discharge measurements were conducted to evaluate the electrochemical properties of the supercapacitors. With the addition of NaI/I₂ mediators, the specific capacitance increased by 27 folds up to 150 F g⁻¹. The specific capacitance increased with increases in the concentration of mediators in the electrodes. The addition of mediators also reduced the electrode resistance and rendered a higher electron transfer rate between mediator and mediator. The stability of the all-solid-state supercapacitor was tested over 2000 charge/discharge cycles.

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1. Introduction

Because supercapacitors (SCs) have a high specific energy than the traditional dielectric capacitors and deliver greater instantaneous power than batteries and fuel cells, they have attracted a lot of attentions recently [1–5]. A supercapacitor may be based on the electrical double layer capacitance (EDLC) of electrode materials with high surface area such as activated carbon, or on the pseudocapacitance originated from redox reactions in active materials. The electrodes of an EDLC are made from carbon materials with a high specific surface area including activated carbon (AC) powder, carbon aero-gel, and carbon nanotube. One major category of electrode materials that give rise to pseudocapacitance is metal oxides including RuO₂ [6,7], MnO₂ [8], NiO [9], and IrO₂ [10]. The second major category of electrode materials is electrical conducting polymers including polyaniline [11–13], polypyrrole [14], and polythiophene [15]. The third major category may be the composites of metal oxides and electrical conducting polymers [16]. One of the most significant development of supercapacitor technology may be the use of nanotechnology to convert these materials in a form of nanostructures (including nanotubes and nanofibers) [17,18].

Another development of the supercapacitor technology is the fabrication of all-solid-state supercapacitors. Advantages of all-

solid-state supercapacitors in comparison to those based on liquid electrolyte include no inherent leakage, the absence of corrosion or combustion, ease of assembly and scale-up, wider temperature range, flexible geometry, and better safety. However, generally speaking, for the same kind of electrode materials, a supercapacitor based on liquid electrolyte seems to possess higher specific capacitance and specific power than a supercapacitor based on solid electrolyte. For example, activated carbon, RuO₂, and electrical conducting polymer based supercapacitors with H₂SO₄ electrolyte can provide a specific capacitance of 320 F g⁻¹ [19], 1170 F g⁻¹ [20], and 608 F g⁻¹ [13], respectively, while those with a sulfonated polymer electrolyte (including Nafion, a proton conducting polymer) can only provide a specific capacitance of 90–130 F g⁻¹ [21], 117–200 F g⁻¹ [22,23], and 98 F g⁻¹ [24]. One of the major disadvantages of these all-solid-state supercapacitors is the low specific power. Saiti and Lufano [21] developed an all-solid-state supercapacitor based on activated carbon, which had a specific power of 0.65 kW kg⁻¹ and a specific capacitance in the range 90–130 F g⁻¹. In the case of RuO₂ based supercapacitor [22], the specific power is even lower. Yamada and Goodenough [25] also developed a RuO₂ and Nafion electrolyte based supercapacitor, which had a specific power of 0.36 kW kg⁻¹ and a specific capacitance of 112 F g⁻¹. However, for liquid electrolyte-based supercapacitors, the specific power is in the range 1.0–10 kW kg⁻¹ while the specific capacitance is much greater. This limits the application of an all-solid-state supercapacitor.

The major reasons for the low performance of all-solid-state supercapacitors may be as follows. Firstly, the ionic conductivity of solid electrolytes is generally much lower than that of liquid

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electrolytes. For example, the commonly used 1 N H_2SO_4 solution (0.5 M) has a conductivity of 0.8 S cm^{-1} while that of Nafion can barely reach 0.2 S cm^{-1} even it is well-treated and fully hydrated. Among the lithium ion conducting polymers, only a few have conductivities above $10^{-3} \text{ S cm}^{-1}$ [26–29]. Secondly, due to insufficient viscosity or fluidity, solid-state electrolytes are usually much more difficult to permeate into the small pores of a porous electrode to form an intimate contact with the electrode surface. The low ionic conductivity and low ion accessibility result in a slow formation of ionic layer with an opposite charge that enables electroneutrality.

Redox pairs (I^-/I_3^- , Co(III)/Co(II) complexes, ferrocene/ferricinium, etc.) have been used in dye-sensitized solar cells as mediators in the liquid and polymer electrolytes for electron transport in the electrolyte and electron transfer at the electrode/electrolyte interfaces [30–33]. It is envisioned that there may be following benefits if the mediators are used as the active materials in a polymer electrolyte based supercapacitors. Firstly, the redox pairs or mediators can store charges via valence changes and electron transfer between the mediators and between the mediators and electronic conductors (e.g. activated carbon) thereby providing extra charge capacity other than EDLC. Secondly, the presence of the mediators in the form of molecules or molecular clusters increases the conductivity of the electrolyte in the porous electrodes via electron transfer between the mediators. Thirdly, each mediator stays in the vicinity of the ions and in the polymer electrolyte. Thus, the accessibility problem of ions to the mediators may be resolved. Finally, the mediators like NaI and I_2 can be acquired at a much lower cost than RuO_2 . After all, it is possible that by doping mediators into polymer electrolytes, not only the total capacitance can be increased but also the maximum power that is inversely proportional to the effective internal resistance can be maximized.

Recently, Lota et al. [34] studied the interface between activated carbon electrodes and liquid electrolyte of 1 mol L^{-1} KI. It was found that iodine based species can actually provide an exceptionally high specific capacitance. For a two electrode assembly, the specific capacitance provided by KI can be $200\text{--}300 \text{ F g}^{-1}$. The authors attributed the performance to the bi-functional effect of the iodide species. That is, to ensure the high ionic conductivity and to provide the pseudocapacitance. The authors also envisioned a great potential for the system because of the huge specific capacitance of the positive electrode, the neutrality of the solution, and good cycle stability. In a recent work [35], the present authors demonstrate that all-solid-state supercapacitors with composite electrodes containing PEO/LiClO_4 and dispersed NaI and I_2 can have a specific capacitance of 210 F g^{-1} , a good self-discharge characteristics and charge/discharge cycle stability. The maximum specific power was 1.5 kW kg^{-1} . In the present research, NaI/I_2 as mediators and active material were added into the mixture of activated carbon and PEO/LiAlO_2 polymer electrolyte to provide the supercapacitor with additional charge storage capacity and enhanced conductivity of the polymer electrolyte in the electrode. This work is focused on the effect of mediator concentration on the performance of the all-solid-state supercapacitors. Thus, $\text{PEO/LiAlO}_2/\text{AC}/\text{NaI}/\text{I}_2$ composite materials with different compositions were used to prepare the electrodes for the supercapacitors. All-solid-state supercapacitors were fabricated using the prepared composite electrodes and a Nafion 117 membrane as a separator. NaI/I_2 mediators were added into the suspension of $\text{PEO/LiAlO}_2/\text{AC}$ to evaluate their effect on the electrochemical performance such as cell resistance, specific capacitance. Long-term charge/discharge cycle tests were conducted to evaluate the cycle stability of the systems. The morphology and crystallinity of the composite electrodes was characterized using scanning

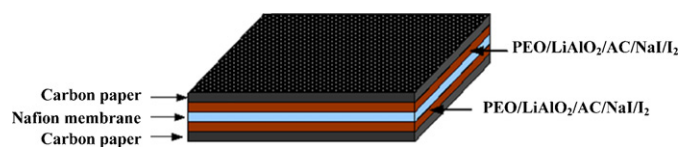


Fig. 1. Schematic of the supercapacitor for electrochemical test.

electron microscopy (SEM) and X-ray diffraction (XRD), respectively.

2. Experimental

2.1. Preparation

2.1.1. Preparation of PEO gel electrolytes

Poly(ethylene oxide) (PEO) powder with an average molecular weight of 400,000 (Sigma–Aldrich) was mixed with lithium aluminate (LiAlO_2) powder (Fluka, $\geq 96\%$) in the weight ratio of 5:1. The mixture was dissolved in solution of acetonitrile (AN, CH_3CN , Sigma–Aldrich) and then was stirred at 60°C in an oven for about 4 h until the suspensions turned into a homogeneous translucent gel. Usually, the mass ratio of acetonitrile solution to the total mass of the mixture of solid components was 10:1.

2.1.2. Addition of iodide/iodine (I^-/I_2) mediators into PEO gel

Sodium iodide (NaI) powder (Alfa Aesar, 99.55%) and iodine (I_2) crystals (Alfa Aesar, 99.8%) were mixed in the molar ratio of 2:1, then dissolved in an aqueous solution with 20% ethanol ($\text{C}_2\text{H}_5\text{OH}$, Sigma–Aldrich, spectrophotometric grade). The solution was added into the PEO gel that was prepared using the procedure stated above. Activated carbon (VULCAN XC72R) powder (Carbot) was added for some samples of the PEO gel. The gel mixture was sonicated for at least 1 h before use.

2.1.3. Preparation of electrode and electrode assembly

A piece of Nanofoam carbon paper was acquired from Marktech International Inc. The specification of the carbon paper was as follows: density, $0.25\text{--}1.0 \text{ g cm}^{-3}$, surface Area, BET $400 \text{ m}^2 \text{ g}^{-1}$, average pore size 0.7 nm. The prepared $\text{PEO/LiAlO}_2/\text{AC}/\text{NaI}/\text{I}_2$ gel was dropped on a piece of Nanofoam carbon paper. After loading with the $\text{PEO/LiAlO}_2/\text{AC}/\text{NaI}/\text{I}_2$ gels, the electrodes on carbon paper were dried naturally in air for about 12 h. To make a supercapacitor assembly, a piece of Nafion117 membrane was immersed in 0.5 M sulfuric acid at room temperature for 2 h. The sandwich of a Nafion117 membrane between two composite electrodes ($1.0\text{--}2.5 \text{ cm}^2$) was pressed at about 4500 psi for 1 min. The supercapacitor assembly is schematically illustrated in Fig. 1.

2.2. Characterization

2.2.1. Composite electrode morphology

The amorphous and crystalline phases of the composite electrodes were analyzed by means of Rigaku XRD using a $\text{CuK}\alpha$ radiation at 40 kV from 10° to 80° at a rate of 2° min^{-1} (2θ). The surface morphologies of the composite electrolyte were investigated using table-top scanning electron microscopy (SEM) (Phenom). All samples were coated with gold using a gold sputtering device before the SEM examination.

2.2.2. Electrochemical measurement

Both electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements were conducted at ambient temperature using solid-state electrochemical cells or supercapacitor assemblies in a form as shown in Fig. 1. The supercapacitor was connected to a potentiostat (Gamry) with a frequency response

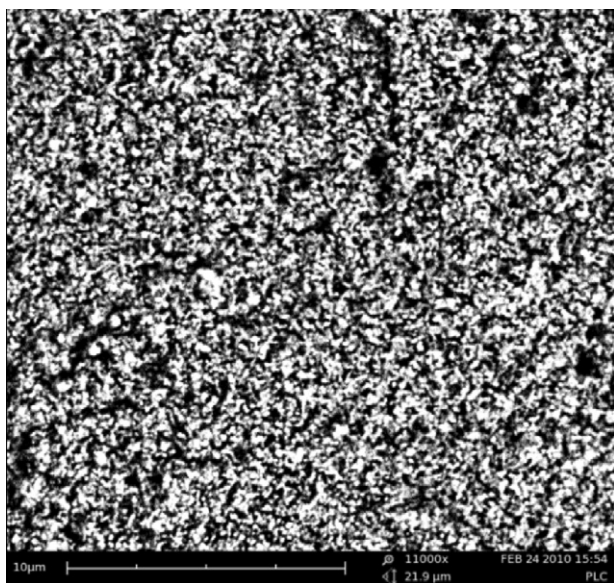


Fig. 2. SEM micrograph of the composite electrode, which is composed of PEO/LiAlO₂, 33 wt% of NaI/I₂, and activated carbon.

analyzer module interfaced to a PC. For the EIS measurements, the applied frequency range was between 1 Hz and 100 kHz, and the amplitude of the sinusoidal voltage was 10 mV. For the CV tests, the potential range was 0.0–0.8 V. Long-term cycle stability was evaluated with charge/discharge tests at a constant current.

In addition to the EIS measurements on the supercapacitor assembly, the lateral or in-plane conductivity of the films was evaluated using a four-electrode AC impedance method which was described in detail in a previous publication [36]. These film samples that contained mediators but did not contain activated carbon were cast from suspensions and let dry.

3. Results and discussion

3.1. SEM and XRD results

An SEM micrograph of a composite electrode is presented in Fig. 2. The composite electrode which is composed of PEO/LiAlO₂, NaI, I₂, and activated carbon show a highly porous structure. An example of XRD pattern of the composite electrode is given in Fig. 3. Although the concentration of NaI/I₂ mediators is 33 wt%, no crystalline NaI and I₂ can be positively identified based on the XRD data. This indicates that the mediators may be in an amorphous structure or in the form of nano-particulates or completely dis-

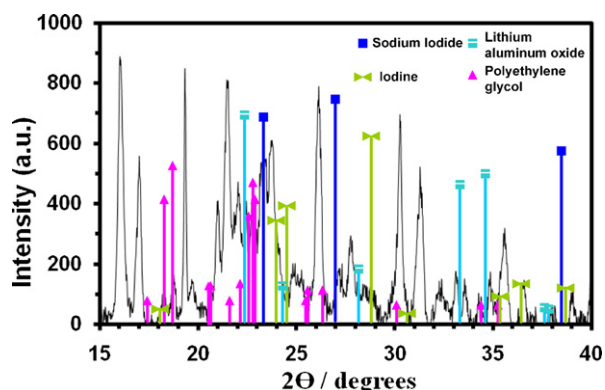


Fig. 3. XRD pattern for PEO/LiAlO₂ doped with 33 wt% of NaI/I₂.

Table 1

The values of conductivity of PEO/LiAlO₂ with or without mediators. The weight ratio of NaI to I₂ is close to 1.0.

Concentration of mediators	Conductivity (S cm ⁻¹)
0.0 wt%	4.45 × 10 ⁻⁵
5.0 wt%	1.02 × 10 ⁻³
10.0 wt%	4.31 × 10 ⁻³
20.0 wt%	5.82 × 10 ⁻³
33.0 wt%	3.87 × 10 ⁻²

solved/dispersed in the PEO/LiAlO₂ electrolyte, which is a desired state.

3.2. Effect of mediator concentration on conductivity

The results of conductivity measurements are listed in Table 1. The conductivity was increased significantly with the addition of the mediators. It is worth mentioning that when iodine is combined with iodide, there will be a fast reaction between them to form triiodide (I₂ + I⁻ ↔ I₃⁻) [37]. Electrons can transfer between three iodine-containing species, I₂, I⁻, and I₃⁻. Thus, the conductivity can be described by the following equation, which is derived from the Dahms–Ruff equation [38]:

$$\sigma = \left(\frac{2e^2}{kT} D_{AX} \right) c_A + \left(\frac{e^2 \delta_{AX}^2 k_{ex}}{3kT} \right) c_A^2 \quad (1)$$

where the subscripts AX and A denote I₃⁻ and I⁻ respectively, D_{AX} is the physical diffusion coefficient, c_A is concentration, δ_{AX} is the center-to-center intersite distance at the exchange reaction, k_{ex} is the exchange reaction rate of the electron transfer reactions. The first term is ascribed to physical transport of the ionized iodine species while the second term is ascribed to electron transfer among the iodine species. For solid-state electrolytes where the mobility of the mediators is very low, the second term dominates the first term.

3.3. Effect of mediator concentration on capacitance

Fig. 4 illustrates cyclic voltammetry results of a supercapacitor with nominally identical electrodes that both contain PEO/LiAlO₂, NaI, I₂, and activated carbon (AC). The composition of each sample is listed in Table 2.

The specific capacitances of the supercapacitors with respect to the mass of the active material (activated carbon and mediators)

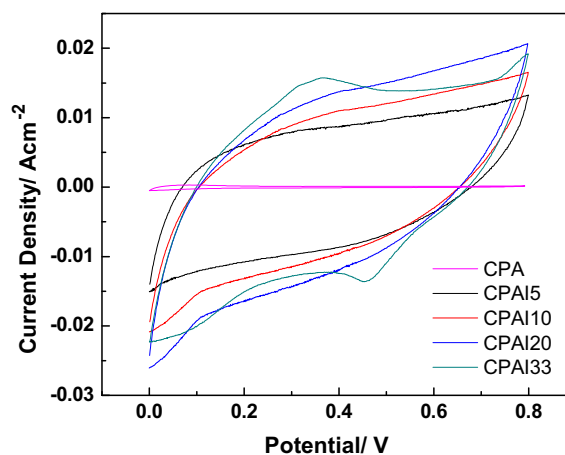


Fig. 4. CV results of symmetric polymer electrode supercapacitors with (CPAI5, CPAI10, CPAI20, CPAI33) and without mediators (CPA) (potential range: 0–0.8 V, scanning rate: 35 mV s⁻¹).

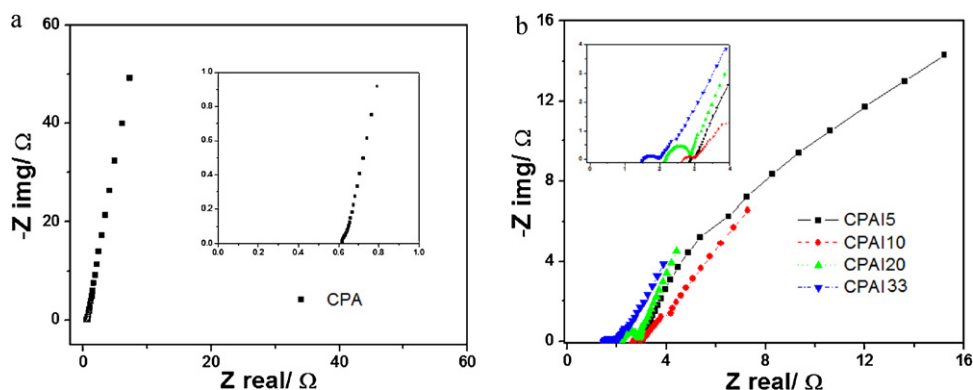


Fig. 5. (a) Nyquist plots for PEO/LiAlO₂/AC electrodes supercapacitor and (b) for PEO/LiAlO₂/AC/NaI/I₂ composite electrodes.

were calculated using the following equations:

$$C_{\text{active}} = \frac{\text{Min}(q_a, q_c)}{\Delta V \cdot m_{\text{active}}} \quad (2)$$

where q_a and q_c are the sums of charge calculated for the anodic and cathodic polarization half cycles, respectively, ΔV is the potential window of the CV test, and m_{active} is the total mass of active materials (activated carbon + mediators), respectively. The specific capacitance values are also listed in Table 2.

The iodine and iodide in aqueous solution may undergo two reactions: (1) $\text{I}_2(\text{s}) + 2\text{e}^- = 2\text{I}^-$ and (2) $\text{I}_3^- + 2\text{e}^- = 3\text{I}^-$. However, in a gel electrolyte, the onset potential for the reactions with respect to the I_3^-/I^- pair is about 0.4 V [37]. No obvious redox peak was observed from the CVs for CPA, CPAI5, CPAI10 and CPAI20. However, a pair of small peaks in the CV for the supercapacitor with the maximum concentration of the mediators (33wt%) was observed. The CV curves for these supercapacitors that do not show obvious redox peak reveal a typical capacitive behavior. The contribution of the activated carbon and carbon electrode to the total capacitance is small.

It is interesting to note that the specific capacitance was increased from 107 to 150 Fg^{-1} when the loading of the mediators was increased from 5 to 33 wt% whereas the specific capacitance of activated carbon was only 5.5 Fg^{-1} . In contrast, previous results on RuO₂ [39] and NiO_x [9] systems indicated that the specific capacitance based on the total mass of RuO₂ and NiO_x respectively decreased slightly when the concentration of the active materials in the electrodes was increased. It is easy to comprehend this phenomenon metal oxides based supercapacitors by assuming that some of the active material (RuO₂, NiO_x, etc.) was not accessible by the ions in the electrolyte. When the concentration of the metal oxides is higher, more active sites in the metal oxides are not accessible. In order to clarify the contributions of the active materials (activated carbon vs. mediators), another test was conducted using an assembly without activated carbon (PAI10 in Table 2).

Table 2
The compositions of the PEO/LiAlO₂/AC/NaI/I₂ composite electrodes.

Sample label	Composition (wt%)					Specific Capacitance (Fg^{-1})
	PEO	LiAlO ₂	AC	I ₂	NaI	
CPA	41.7	8.3	50	0	0	5.50
PAI10	72	18	0	5.0	5.0	82
CPAI5	39.6	7.9	47.5	2.5	2.5	107
CPAI10	37.5	7.5	45.0	5.0	5.0	120
CPAI20	33.3	6.7	40.0	10.0	10.0	134
CPAI33	28.3	5.7	33.0	16.5	16.5	150

This assembly contained 10 wt% mediators, 72 wt% PEO and 18 wt% LiAlO₂. The specific capacitance for this assembly was 82 Fg^{-1} . Based on the specific capacitances for activated carbon and mediators, the CPAI10 assembly should have a specific capacitance of 87.0 ($0.9 \times 5.5 + 1.0 \times 82$) Fg^{-1} , which is significantly less than the measured value of 120 Fg^{-1} . Thus, the present results revealed that there is a cooperative effect of the electrode components, electrolyte, activated carbon and mediators. The electron transfer rate between the mediators which is described by the second term in Eq. (1) during a charge/discharge process is proportional to the square of the concentration. Hence, the electron transfer among the active materials is more difficult at a lower concentration than at a higher concentration. Thus, unlike the case for the other types of supercapacitors where ion access/transport to the active materials/sites dominates the charge/discharge process, in the present supercapacitors, where the mediators are dispersed among ions in the solid electrolyte, the electron transfer between the mediators and between the mediators and carbon dominates the charge/discharge process.

Nyquist plots for the supercapacitors described in Fig. 4 are shown in Fig. 5. The Nyquist plot for the electrode without mediators is typical for an EDLC [40,41]. The Nyquist plots for the supercapacitors with PEO/LiAlO₂/AC/NaI/I₂ composite electrodes show arcs in the high frequency region and straight lines in the low frequency region. Increasing the concentration of the mediators results in reduction of the series resistance which is the sum of the resistance of the separator, the contact resistance, the ionic resistance and electronic resistance in the electrodes [42]. The small semi-circles indicate that the charge transfer resistance in the system is low ($\sim 0.5 \Omega$). The tails at the low frequency range have similar slopes, which are probably due to the transport in porous electrode (Warburg impedance) [40,41].

3.4. Effect of scan rate

In order to evaluate the charge/discharge response of the supercapacitors, CV measurements were conducted under a range of scan rates. Fig. 6 shows the CV curves obtained with potential scan rates from 20 to 200 mVs^{-1} for a symmetric supercapacitor with PEO/LiAlO₂/AC/NaI/I₂ supercapacitor.

In Fig. 6, the shape of the CVs for the supercapacitor with mediators is similar to those observed for other systems with a capacitive behavior. Addition of NaI/I₂ mediators increases the capacitance by contributing pseudocapacitance, which is much greater than that of EDLC, to the total capacitance. The relationship between the scan rate and the maximum current density are illustrated in Fig. 7. Thus for the range of scan rates of supercapacitors, in particular an EDLC,

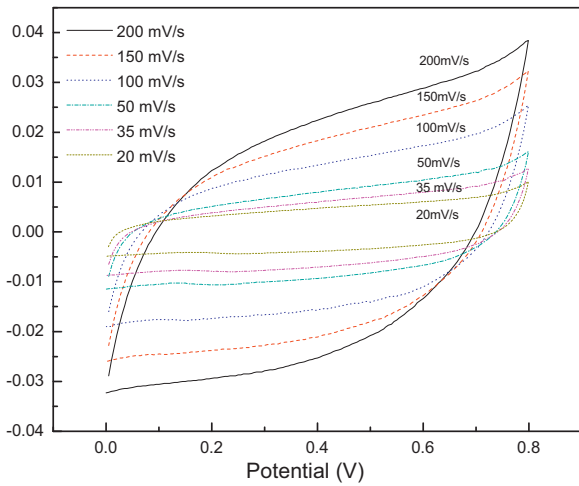


Fig. 6. CV results as a function of potential scan rate for a symmetric supercapacitor with 5.0 wt% of mediators in electrode (CPAI5).

the current can be described by [40]:

$$I = \frac{dQ}{dt} = \frac{dQ}{dE} \times \frac{dE}{dt} = \nu C \quad (3)$$

where I is the current density, ν is the scan rate, dQ , dt , and dE are the differentials of charge, time, and potential. The charge current is proportional to the scan rate, which is typical for an EDLC [40]. This is considered as a desired behavior for the systems with pseudocapacitance including RuO_2 based supercapacitors. The capacitance evaluated using the slope is 83.0 F g^{-1} for the SC with mediators or 7.0 F g^{-1} for the SC without mediators.

3.5. Effect of cycle number

The cycle stability and durability of the supercapacitors were evaluated using galvanostatic charge/discharge tests. These tests were conducted by first charging a supercapacitor at a constant current density of 3 mA cm^{-2} while recording the potential increase and then reversing the current to discharge the supercapacitor at a constant current.

Fig. 8 shows the cycling stability of the symmetric $\text{PEO/LiAlO}_2/\text{AC}/\text{NaI}/\text{I}_2$ composite electrodes supercapacitor at room temperature. The specific capacitance of the symmetric $\text{PEO/LiAlO}_2/\text{AC}/\text{NaI}/\text{I}_2$ electrode supercapacitor capacitance

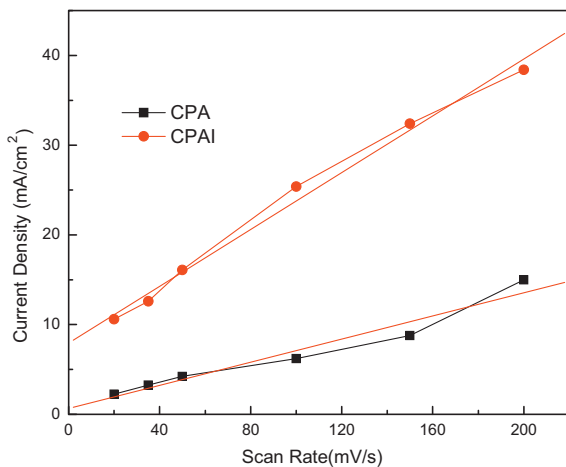


Fig. 7. Limiting current density plotted versus scan rate (the electrode potential is 0.8 V). CPA: a SC without mediators. CPAI5: a SC with mediators concentration of 5.0 wt%.

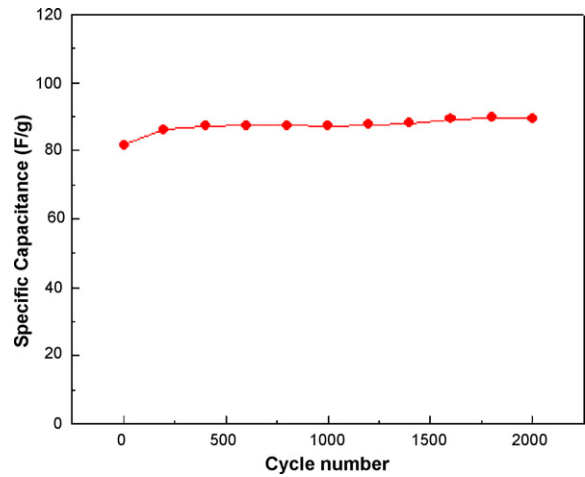


Fig. 8. Specific capacitance as a function of charge/discharge cycle numbers for $\text{PEO/LiAlO}_2/\text{AC}/\text{NaI}/\text{I}_2$ -Nafion- $\text{PEO/LiAlO}_2/\text{AC}/\text{NaI}/\text{I}_2$ supercapacitor. The concentration of mediators in the electrode is 5.0 wt%.

increased from 80 F g^{-1} to 84 F g^{-1} in the first 200 cycles and then slowly increased to 90 F g^{-1} between 200 and 2000 cycles. This slight capacitance increase may be due to the improvement of the mediators distribution caused by the charge/discharge processes.

4. Conclusions

$\text{PEO/LiAlO}_2/\text{AC}/\text{NaI}/\text{I}_2$ -Nafion- $\text{PEO/LiAlO}_2/\text{AC}/\text{NaI}/\text{I}_2$ -based all-solid-state supercapacitors were fabricated by depositing $\text{PEO/LiAlO}_2/\text{AC}/\text{NaI}/\text{I}_2$ slurry on nanofoam carbon paper, then assembling two identical electrodes on both side of Nafion 117 membrane. The cell resistance, specific capacitance, specific power, specific energy, and cycling stability were evaluated via EIS, CV, and galvanostatic charge/discharge methods.

With the addition of NaI/I_2 mediators, the specific capacitance increased almost 27 folds with respect to that of a supercapacitor without mediators. The stability of the supercapacitor specific capacitance was confirmed within 2000 cycles in which no significant specific capacitance decrease is observed for the supercapacitors with mediators. The addition of mediators not only reduces the electrode resistance of the supercapacitor, but also provides the supercapacitor with pseudocapacitance. Increasing the active materials (activated carbon and mediators) increases the specific capacitance of the all-solid-state supercapacitors. A cooperative effect of the electrolyte, activated carbon and mediators in the electrodes was observed.

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