PAPER

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IOP Publishing Smart Materials and Structures
Smart Mater. Struct. **28** (2019) 054003 (9pp) https://doi.org/10.1088/1361-665X/ab1182

Ionic polymer metal composites for use as an organic electrolyte supercapacitor

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Received 4 December 2018, revised 8 March 2019
Accepted for publication 20 March 2019
Published 18 April 2019

Abstract

Choosing the right electrolyte for enhancement in energy storage and dissipation efficiencies of an electrochemical supercapacitor is a critical decision and a successful material choice could solve many issues faced by renewable energies such as wind and solar energy. Traditional aqueous electrolytes have been and continue to be used for their excellent electrolytic performance, but over past few decades, use of solid polymer electrolytes (SPEs) improved the performance of such devices by enhancing the power density and energy density. Platinum (Pt) incorporated ionic polymer metal composites (Pt-IPMCs) are being investigated for their applicability as solid polymer electrolyte (SPE) membrane for high-power supercapacitors as they have demonstrated improved performances in devices such as fuel cells, soft actuators etc. Pt nanoparticles were dispersed into a cubical Nafion membrane in a dense cluster (size distribution showing narrow). The Pt-IPMCs were tested using lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate ($(CH_2O)_2CO$) and ethyl-methyl carbonate ($C_4H_8O_3$) mixed in 2/1 volumetric ratio. Pt-IPMC resulted a lower internal voltage drop (0.15 V), higher ionic conductivity (0.46 mS cm^{-1}), and higher specific capacitance (50.9 F g^{-1}) compared with the commercial liquid electrolytes or Nafion 117. The average power density and energy density have improved by 19 and 17%, respectively by using Pt-IPMC electrolyte which could be ascribed to the decrease in the cell resistance or the increase of ionic conductivity. It should be noted that IPMC can be adopted as supercapacitor as well as soft actuator.

Keywords: IPMC, Supercapacitor, solid polymer electrolyte

(Some figures may appear in colour only in the online journal)

1. Introduction

Supercapacitors or ultracapacitors are the electrochemical devices, that have high charge/discharge rate, high power density, and excellent durability [1, 2]; and are currently the focus of academia and industry due to their potential applications in diverse fields. Supercapacitors and similar electrochemical devices typically use aqueous/liquid electrolytes and are now moving towards using solid polymer electrolytes (SPEs), since they are at micron level thickness, they significantly reduce the weight of the cell and can enable systems to be lighter, safer and flexible for device assembly and utilization, in comparison to electrolyte systems [3, 4]. Various SPEs, such as poly(methyl methacrylate), poly(acrylonitrile), and poly(ethylene oxide)-based gel electrolytes, are being considered for application in supercapacitors by various research groups [5–7]. Although they have a promising future, research indicates that SPEs tend to have low ionic

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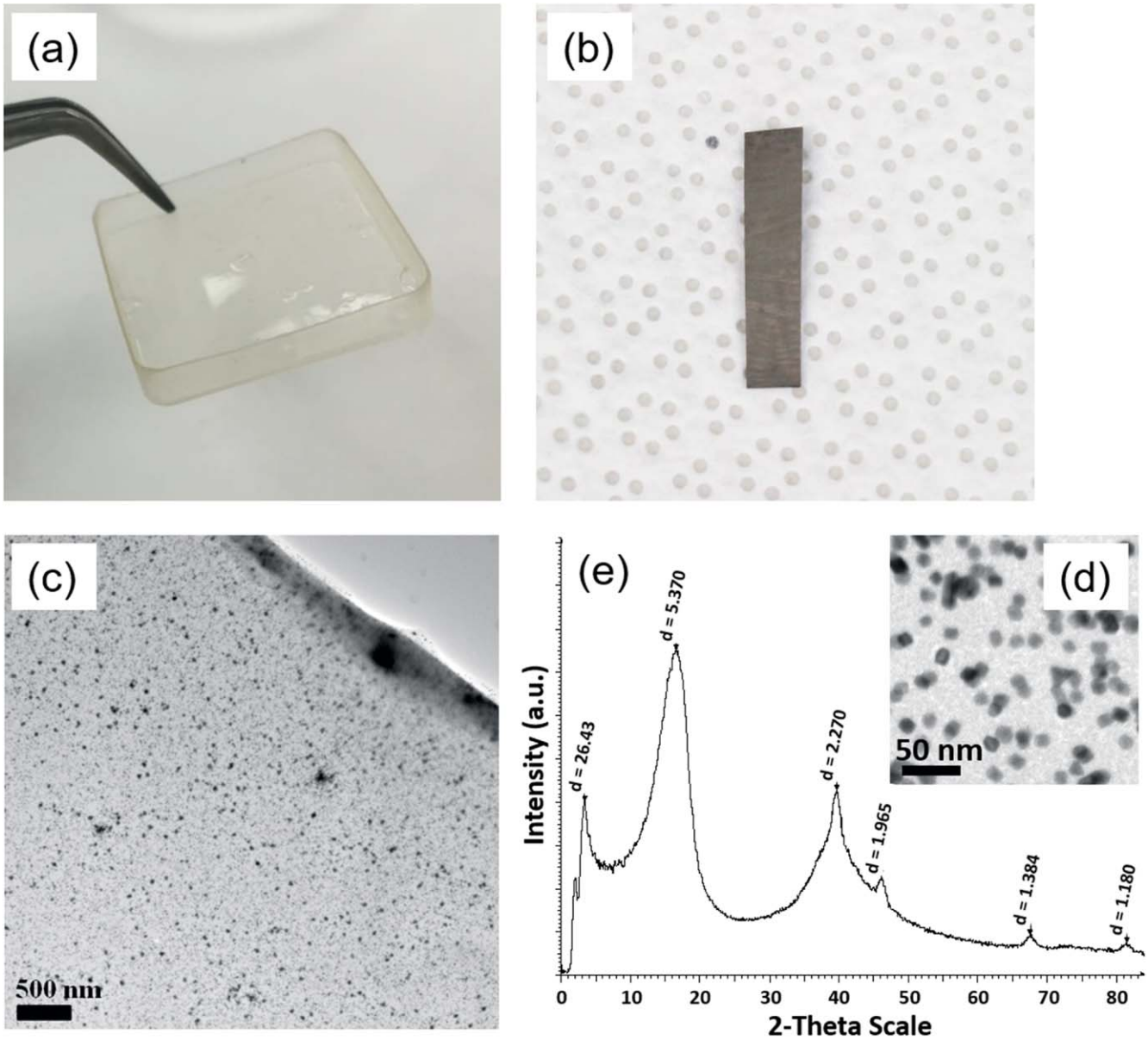

Figure 1. Photographs of recast Nafion film before (a) and after (b) reduction process. TEM results of Pt nanoparticles in the recast Nafion membrane (c) and (d) and x-ray patterns of the selected area (e).

conductivity (10^{-4} to 10^{-3} S cm^{-1}) at room temperature, which subsequently decreases their internal resistance and thus decreased performance as a capacitor.

Ionic polymer metal composites (IPMC) are one of the prominent electroactive polymer materials that have been used in the fields of energy conversion (e.g., direct methanol fuel cells), biomedical (for drug delivery), soft robotics (in actuation and sensing) and are now being considered as a potential electrolyte membrane for supercapacitors, owing to their unique operation under low voltage and their sensing capabilities [8]. The structure of IPMC comprises an electroactive polymeric membrane that is sandwiched between metallic layers (see figures in appendix). Platinum (Pt) or gold are the metals that are coated on to the membrane as they have improved the ionic conductivity [9]. Among commercially available ion exchange membranes, Nafion (developed by DuPont) is the leading choice and the structure and properties of this perfluorinated ionomer has been extensively studied [10–16].

Nafion membrane is comprised of clusters (ca. 5 nm diameter) of sulfonated perfluoroalkyl ether groups interlinked by small channels [17, 18]. Nafion membranes typically manufactured by extrusion. Also, they can be recast using a liquid form of Nafion. Even though commercialized extruded Nafion films have excellent electrochemical properties, recast Nafion membranes have a slight variation of the properties and morphologies [19, 20]. These recast Nafion membranes have an increased liquid uptake than the commercial membranes due to their different swelling behavior and ionic conductivities [20]. Particularly, Lufrano *et al* have examined Nafion based electrolytes for a carbon-based (electrical double layer capacitor) EDLC super capacitor in

aqueous electrolyte (sulfuric acid), where the specific capacitance was reported to be about 90 F g^{-1} [21]. Currently, IPMCs are being extensively investigated for being used in water-based media (electrolytes) and we believe that applying IPMCs (specifically using organic electrolytes) for electrochemical energy storage application would produce results that could enable us to design an efficient device that is durable. Organic electrolytes are a preferable media for energy storage devices because of their larger break down voltage in comparison to aqueous electrolytes. Typically, aqueous electrolytes have a breakdown voltage of 1 V, hence their operating voltage restricts the cells performance in the aspects of power density and storage capacitance.

Since supercapacitors are being used for storage and discharge applications, operating voltage (V) has a significant role in determining their performance as energy storage capacity and output power are proportional to V^2 and V, respectively [22]. The typical operation voltage of organic electrolytes (2.5∼3.7 V) is higher than aqueous electrolyte systems (∼1.2 V) due to the electrochemical stability of organic electrolytes and thus are preferable for improved supercapacitor performance. Furthermore, wide potential (or voltage) window of organic electrolytes facilitates flexibility in supercapacitor module design and assembly, for instance, the number of series/parallel connections could be changed until desirable outcome is achieved. Similarly, control of total equivalent series resistance (ESR), and voltage-drop of individual cell as well as integrated modules could lead to versatile applications [23]. However, it should be noted that the ionic resistance of organic electrolytes is often an order of magnitude higher than aqueous systems and may limit the power capability of the supercapacitors.

Ionic conductivity of an electrolyte is closely related to the internal resistance (IR) of the cell, which shows that the cell performance is dependent on IR. Power density of the cell is inversely proportional to the IR and therefore power density decreases as the resistance increases. It was demonstrated that the Nafion membranes modified by the incorporation of metal nanoparticles changes the ionic conductivity and electrochemical properties selectively [24–26] and such metal electrodes with a nano dispersed structure would provide a high capacitance [27]. More specifically, when the Pt nanoparticles are formed inside the membrane, the proton conductivities of modified membrane increased due to the proton adsorption on the surface of the loaded Pt nanoparticles and the increased cluster size of Nafion [26].

In this study, the electrochemical characteristics of the Nafion-based SPEs and Pt-IPMCs were investigated in organic-electrolyte supercapacitor systems. Pt nanoparticles were successfully incorporated in the Nafion membrane through the ion exchange (the cationic Pt) ligand on the sulfonic groups in the hydrated ionomer. These Pt-IPMCs were tested for supercapacitor application as they have improved ionic conductivity, energy density, capacitance, and power density. These studies have provided results that reinforce our hypothesis, as we have successfully demonstrated that Pt-IPMC's have showed a meaningful improvement of energy and power density in comparison to

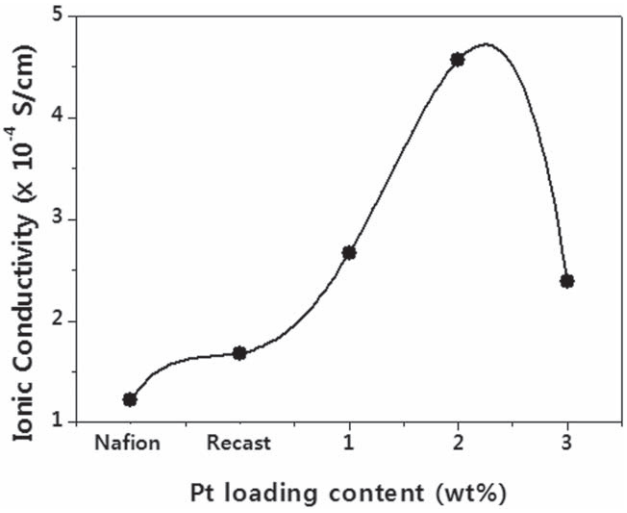

Figure 2. Conductivity of the Pt-IPMCs at different loadings of Pt.

electrolytes currently being used. Particularly, the results are very encouraging with 2 wt% of Pt loading. With the increasing demand for high power density, quick charge-discharge capability, higher energy density, IPMC's would be a viable candidate with the potential to overcome the issues faced by conventional supercapacitors with their efficient and economic electrochemical properties.

2. Results and discussion

The Nafion membrane was prepared by casting of Nafion solution for overnight. Recast membranes were acid cleaned. The next step, primary plating is an impregnation-reduction process on the inner surface of the membranes. Nafion membranes were soaked in a Pt (II) salt solution and rinsed with DI water several times. To metalize the surface of the membranes, they were immersed in an aqueous solution containing NH_4OH and $NaBH_4$. Figures 1(a) and (b) show the images of recast Nafion membrane before and after Pt reduction process. It can be noticed that there is a coating of the platinum nano-particles that were embedded into the Nafion membrane. Figures 1(c) and (d) show the TEM images of Nafion membrane after reduction process. There is a uniform dispersion and coating of the pt nano particle throughout the membrane. Figure 1(e) presents the x-ray diffraction pattern demonstrates that Pt nanoparticles have successfully formed in the Nafion membrane. In our previous study, we confirmed that Pt nanoparticles could be synthesized in the restricted space of the hydrated cavity of the Nafion membrane, because the growth of Pt-particle is geometrically restrained by the fluorinated hydrophobic phase. Similarly, the recast Nafion membrane shows well-dispersed Pt nanoparticles demonstrating that the cationic Pt complex ($[Pt(NH_3)_4]^{2+}$), is immobilized in the hydrophilic cavity of the SO_3^{2-} groups due to the ion-dipole interaction [26]. During the reduction process, Pt nanoparticles may very well grow in the confined hydrophilic cavity of Nafion, and the corresponding dimensions of the cavity are known to be 4.7, 13.1,

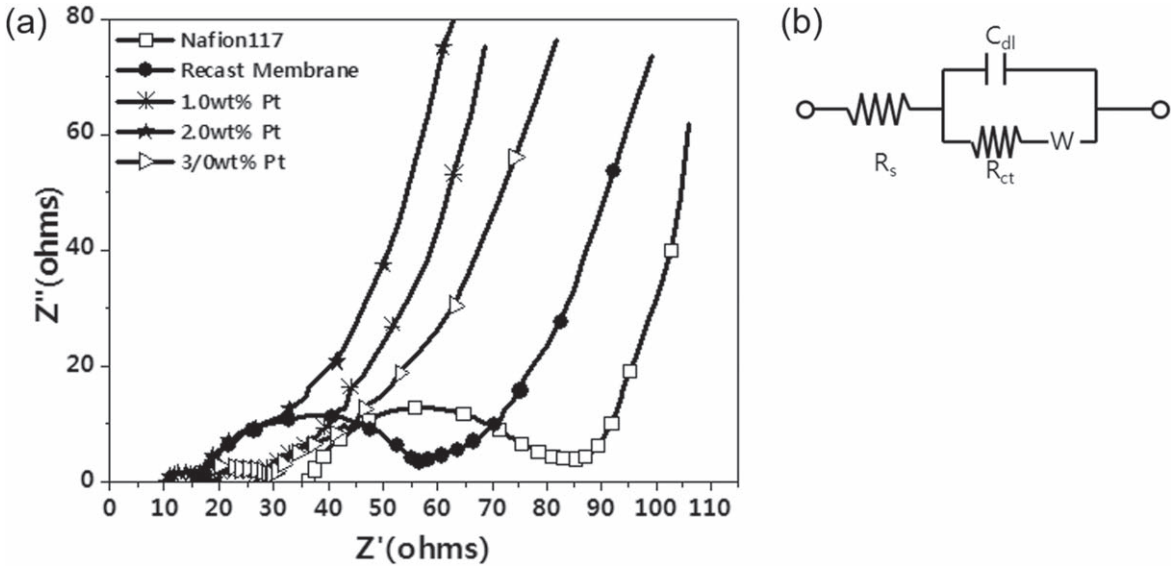

Figure 3. (a) Nyquist plot of supercapacitors with Nafion 117, recast membrane, and Pt-IPMCs (1.0, 2.0, and 3.0 wt%) and (b) diagram of Randles circuit.

and 12.9 nm for Pt contents of 1, 2, and 3 wt%, respectively [26, 28], resulting in uniform-sized and well-dispersed Pt particles. As can be seen in figure 1(d), the examination of their 3-dimensional structure shows that a cubic shape of Pt nanoparticles. Figure 1(e) shows x-ray diffraction patterns attributed to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) diffractions of the Pt face-centered cubic crystal structure.

The ionic conductivity of the Pt-IPMCs shows substantially higher than that of the pristine Nafion 117 membrane as observed in figure 2 which shows the ionic conductivity of the Pt-IPMCs at different Pt content. Similarly, there is a noticeable increase in the ionic conductivities with the introduction of Pt nanoparticles, which is evident from the 0.12 mS cm^{-1} conductivity in pristine Nafion and the 4-fold increment of the ionic conductivity with a value of 0.46 mS cm^{-1} in the 2 wt% Pt-IPMC. This enhancement in the ionic conductivity is likely related to the electrolyte uptake and size of the clusters [20], and there is a great possibility that the rearranged morphology of the clusters results in a higher ionic conductivity. However, when the Pt loading becomes excessive, as in the case of 3 wt% Pt in figure 2, the hydrated clusters encounter squeezing forces on the cluster volume because of the neighboring Pt nanoparticles and, thereby, the electrolyte uptake and the ionic conductivity of the recast Nafion membrane are decreased at very high concentration of Pt nanoparticles.

The impedance spectra of the supercapacitor cells using the synthesized Pt-IPMCs were measured in the frequency range from 10 mHz to 100 kHz (shown in figure 3(a)). The impedance spectrum of the cell has a semicircle and a line inclined towards the real axis. Obtained Nyquist plot demonstrates that the system behaves like a RC circuit with R (electrolytic resistance) and C in parallel at high frequencies which is justified by the presence of semicircle. Figure 3(b) shows the Randles circuit, is a practical method of modeling

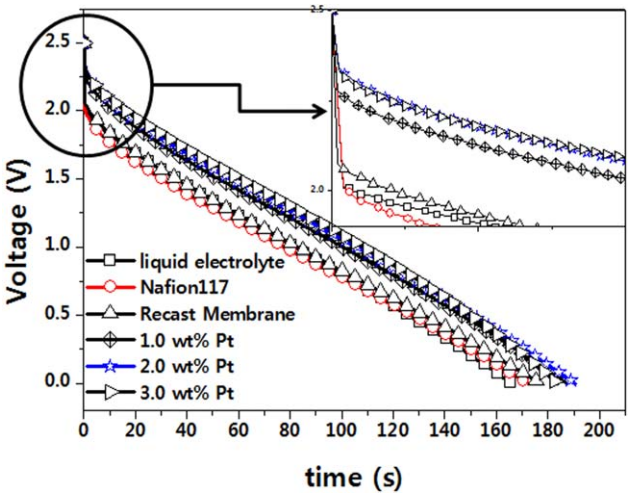

Figure 4. Discharge curve of the supercapacitors assembled with liquid electrolytes, Nafion, and Pt-IPMCs measured from 0 to 2.5 V at 5 mA s^{-1}.

an electrochemical cell as an equivalent circuit [29, 30]. W represents Warburg diffusion element, R_s is the electrolyte resistance, R_{ct} is the polarization resistance, and C_{dl} is the double layer capacitance. The sharp increment of Z″ (imaginary part) in the impedance spectra at low frequencies is explained by capacitive behavior of the electrode. The ESR is the sum of the various contributions including the electrolyte resistance, the ionic resistance of the ions moving through the separator, the diffusion resistance of the ions moving in the small pores, the contact resistance between the active electrode material and the current collector [31]. The ESR (resistance at 1 kHz) of the Pt-IPMCs shows lower value than that of the pristine Nafion. For example, the ESRs of the supercapacitor cells with pristine Nafion membrane is 56 Ω

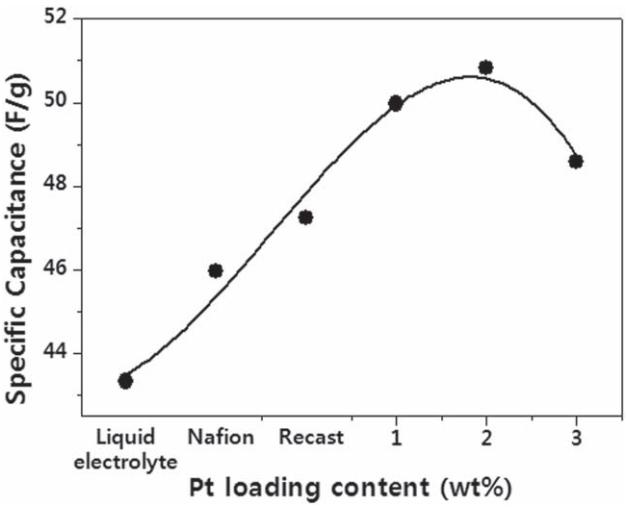

Figure 5. Specific capacitance of the supercapacitors plotted as a function of the Pt loading.

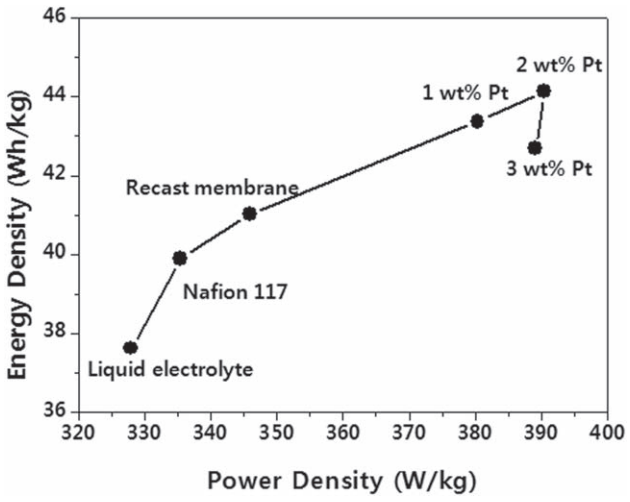

Figure 6. Average power and energy density for supercapacitors prepared with Pt-IPMCs between 0 and 2.5 V with cycling current density of 5 mA s^{-1} with varied Pt loading.

and for the 2 wt% Pt recast Nafion film, it is 15 Ω. This could be attributed that the ionic conductivity and electrolyte uptake of the latter are higher than those of the former. Additionally, the electrolyte resistance of Pt-IPMCs is 10 Ω, which is compared with the corresponding value of 36 Ω for the pristine Nafion film (72% decrease in the electrolyte resistance).

Figure 4 compares the discharge curves of the supercapacitors prepared of the liquid electrolyte and the Pt-IPMCs at different loadings of Pt. Samples are fully charged up to 2.5 V and waiting for 240 s before start testing. The discharging time of the supercapacitors composed of the Pt-IPMCs is over 180 s, while the supercapacitors prepared of the liquid electrolyte and Nafion 117 membrane shows around 160 s. The initial voltage drop is ascribed to the ohmic loss during the discharge process caused by the IR of the supercapacitor and is measured to be 0.15 V for the Pt-IPMCs containing 2 wt% and 0.49 V for the liquid electrolyte system. The results of IR value agree with those measured in the impedance spectra (figure 3), giving impedance resistances lower than the ones obtained from the IR drops, which is usually observed in supercapacitor analysis. It should be noted that the high voltage drop effected by the internal resistance indicates a low capacitance and poor cell performance in supercapacitors [32].

Figure 5 shows the specific capacitance of the Pt-IPMCs supercapacitors with varied Pt loadings. Specific capacitance of the cells using Pt-IPMC electrolyte are noticeably higher than those of the cells using liquid electrolyte or the ones using pristine Nafion membrane. The liquid electrolyte system has 43.3 F g^{-1} of specific capacitance and for the polymer electrolytes at a Pt loading of 2 wt% shows as high as 50.9 F g^{-1}. This suggests that the polymer electrolytes system has lower the resistance than that of the liquid electrolyte system (see in figure 4). In addition, the specific capacitance of the recast membrane system (47.3 F g^{-1}) is higher than that of the pristine Nafion system (45.9 F g^{-1}) due to the increased size of the clusters and its lower ionic resistance. The maximum value of the specific capacitance appears at a Pt loading of 2 wt% which is due to the increase in water uptake which enhances the ionic conductivity. At the 3 wt% Pt IPMC, it has been theorized [26] that the platinum particles squeeze the cluster volume and this reduces the water uptake and corresponding decrease of ionic conductivity and specific capacitance are resulted.

The average power density (P_{av}) and energy density (E) could be estimated from the voltage, current, and capacitance as follows:

$$P_{av} = \frac{1}{2} I \cdot V_i \tag{1}$$

$$\mathrm{E} = \frac{1}{2} C V^2 \tag{2}$$

Where I is the stable current, V or V_i is the initial voltage, and C is the capacitance. Figure 6 shows the average power density versus the energy density of the SPE systems investigated in this study. Theoretical prediction of power density (given by equation (A.1)) is indicating that the average power density is dependent on the initial voltage and equivalent ESR (or the IR drop). From figure 6 note that the average power density increases from 346 to 390 W kg^{-1} as the Pt loading is increased from 0 to 2 wt%. This increment in the power density is attributed to the decreased IR drop (see figures 3 and 4). Equation (A.2) shows that energy density is related to the cell capacitance and the initial voltage in a proportional fashion. Accordingly, the average power density and energy density of the Pt-IPMCs containing 2 wt% of Pt reaches 390 and 44.1 Wh kg^{-1}, as compared with 328 and 37.6 Wh kg^{-1} of the liquid electrolyte system, representing increases of 19 and 17%, respectively. As seen in this Ragon plot, the recast 2 wt% Pt-IPMCs substantially increases the power-energy performance of the supercapacitors as compared with either the commercialized liquid electrolyte or Nafion 117 membrane.

Table 1. Summary of results of this work, compared with commercial aqueous electrolyte and Nafion membrane.

Electrolyte	Equivalent series resistance (Ω)	Electrolyte resistance (Ω)	Initial voltage (v_i)	Ionic conductivity (mS s^{-1})	Specific capacitance (F g^{-1})	Power density (W Kg^{-1})	Energy density (W Kg^{-1})
Liquid electrolyte	—	—	2.01	—	43.3	328	37.6
Pristine Nafion	56	36	2.01	0.12	45.9	335	39.8
Recast Nafion	41	18	2.08	0.17	47.3	346	40.9
Pt-IPMC (1 wt% Pt)	26	18	2.28	0.26	50.1	381	43.2
Pt-IPMC (2 wt% Pt)	15	10	2.34	0.46	50.9	390	44.1
Pt-IPMC (3 wt% Pt)	28	13	2.34	0.24	48.7	389	42.3

Overall, the Pt-IPMCs systems demonstrated excellent performance of electrochemical characteristics, with a higher power and energy density, compared to the commercial liquid electrolyte systems (table 1). This trend is more pronounced for the 2 wt% Pt- IPMC in this study, with a low resistance or enhanced ionic conductivity and this it can be concluded that the 2 wt% Pt-IPMC has the best potential to be used as an electrolyte in a supercapacitor cell. These encouraging results boosts the confidence in the applicability and capability of polymer electrolytes membrane systems, for a more reliable, efficient and safer supercapacitor modules for the upcoming markets of electric vehicles and other systems that use high-power energy storage devices.

3. Conclusions

The study of the electrochemical properties of Pt-IPMCs provided significant results that are encouraging and provide data that supports the use of these IPMCs as an electrolyte membrane for obtaining improved performance of supercapacitors with high power and energy densities. Incorporation of Pt nanoparticles into the Nafion membrane decreases the IR and this drop leads to an Ohmic loss smaller than 0.15 V (for 2 wt% Pt-IPMC), which is very small compared to the commercial liquid electrolytes and pristine Nafion, for which the Ohmic losses are 0.49 and 0.48 V, respectively. In the discharge measurements of the supercapacitors, the energy density was enhanced (17%) compared to the liquid electrolyte system. As the need for energy generation and storage increases with the growing needs of human, more efficient energy storage devices will play an important role in defining the quality of life and using the right electrolyte could make a difference. Thus, from the study we have conducted, use of Pt-IPMC as a solid electrolyte membrane can be encouraged and further studies on the properties of such membranes could reveal the avenues for improvement and leading to increased applications for efficient systems that could ultimately benefit the society.

Acknowledgments

This research was supported by the WCU (World Class University) program (R31-2008-10029) and the research grant (2010-0028939) through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology. We also appreciate the project and equipment support from Gyeonggi Province through the GRRC program in Sungkyunkwan University. KJK thanks the partial financial support from Office of Naval Research (N00014-16-1-2356).

Appendix

Experimental procedure

Following a typical synthesis route [26, 28], 10 g of Nafion solution (5 wt% solution in lower aliphatic alcohols/H_2O mix, Aldrich) was added to an alcoholic solvent at room temperature. Then Tetraammineplatinum(II) chloride ($[Pt(NH_3)_4]Cl_2$) salt was added to this mixture at various concentrations to give Pt loadings of 1, 2, and 3 wt%. Subsequently, the solution was cast and dried in a vacuum oven. After the complete reduction of the Pt ions to Pt using sodium borohydride solution, this film was washed with DI water several times to eliminate any other contaminants/residual ions. The morphology of the Pt nanoparticles was observed by high-resolution transmission electron microscopy (HR-TEM: JEM2100F, JEOL). The organic electrolyte containing 1.0 M Lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate ($(CH_2O)_2CO$) and ethyl-methyl carbonate ($C_4H_8O_3$) mixed in 2/1 volumetric ratio which was purchased from Cheil Industries Co., Korea. The membranes were immersed in organic electrolyte for 2 h to prepare polymer electrolyte (containing Pt nanoparticles).

The ionic conductivity of the polymer electrolytes was investigated by the AC impedance method using a impedance/gain-phase analyzer (SI 1260, Solartron Co.). The ionic conductivity (σ) of the polymer electrolytes was evaluated as follows:

$$\sigma = \frac{d}{Rs * A} \tag{A.1}$$

where d is thickness, R_s is the electrolyte resistance, and A is surface area of the polymer electrolytes, respectively. The electrolyte resistance was recorded during the impedance test by placing the separator and the electrolyte between the platinum electrodes.

The electrodes were prepared by bar-coating on aluminum (Al) foil with slurry containing the activated carbon (Norit Co.), graphite (Timkal Co.), binder (Nafion solution) and ethanol. The diameter and thickness of the electrode was 15 mm and 240 μm, respectively. The supercapacitor cell was prepared by sandwiching the two carbon electrodes with the polymer electrolytes or liquid electrolyte with polyolefin separator (Celgard, USA), and then cell was enclosed using an Al coin cell and sealed.

Cyclic voltammetry (WonA tech Automatic Battery Cycler) was performed to investigate the charge-discharge characteristics of the supercapacitors. The capacitance of the prepared cells was determined using the following equation [33]:

$$\mathrm{C} = \frac{I\Delta t}{\Delta V} \tag{A.2}$$

Microscopic images of Pt-IPMC

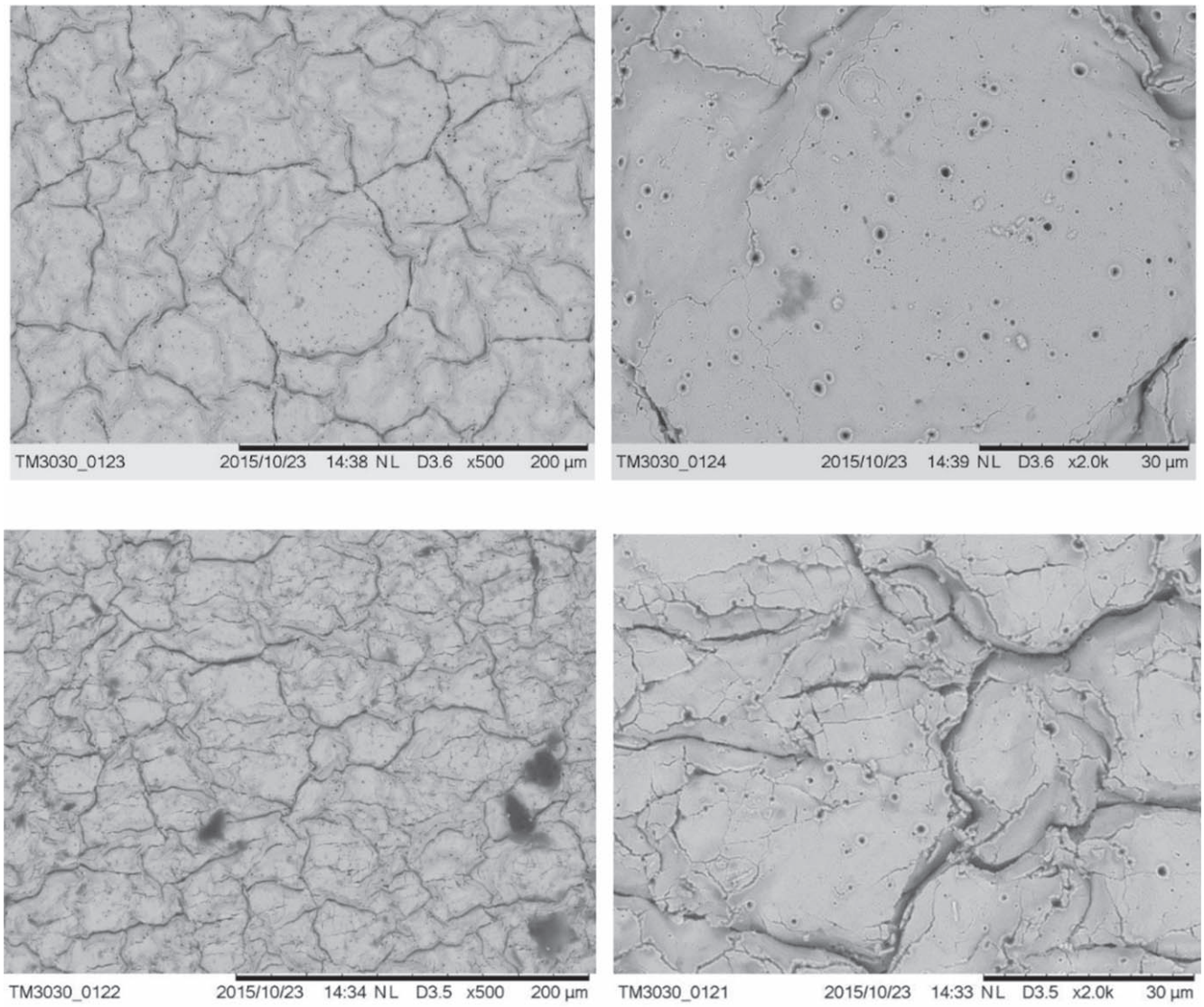

Figure A1. SEM microscopic images of typical Pt-IPMCs (surface images); Top-IPMC prior to actuation test; bottom-IPMC showing cracks after actuation/deformation testing.

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