Electrochromic Supercapacitor Based on Ion Gel Electrolytes

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Introduction

Electrochromic Supercapacitor (ECS)

- It is a device that takes advantage of the similarity of the composition and principles of the EC device to the supercapacitor, a electrochemical energy device.
- ECS developed in this study is one of the promising devices for multifunctional electronics due to high power density and outstanding cycle stability.

Table 1. ECD world market trend

	2014	2015	2016	2017	2018	CAGR (14~18)%
EC Display	25	40	60	80	100	41.4
Electronic Shelf Labels	192	225	266	317	380	18.6
EC Rearview Mirror	1,984	2,409	2,924	3,534	4,166	20.4
EC Smart Window	21	29	40	61	95	45.8
Total	2,223	2,703	3,289	3,992	4,742	20.8

Ion gel electrolyte

- The form of an ionic liquid + a copolymer forming a three-dimensional structure.
- It have not only good electrical properties of an ionic liquid, but also high stability and mechanical properties of solid polymer electrolytes.

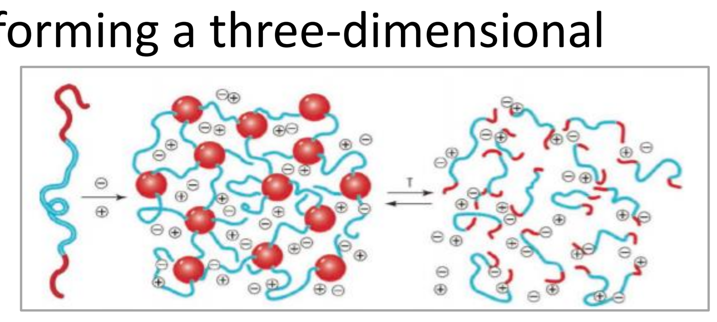


Figure 1. Structure of ion gel obtained through the blend of ionic liquids and ABA-type triple block copolymer

- Performance depends on the mixing ratio of copolymer and ionic liquid.

Results & Discussion

PS-r-PMMA + [EMI][TFSI]

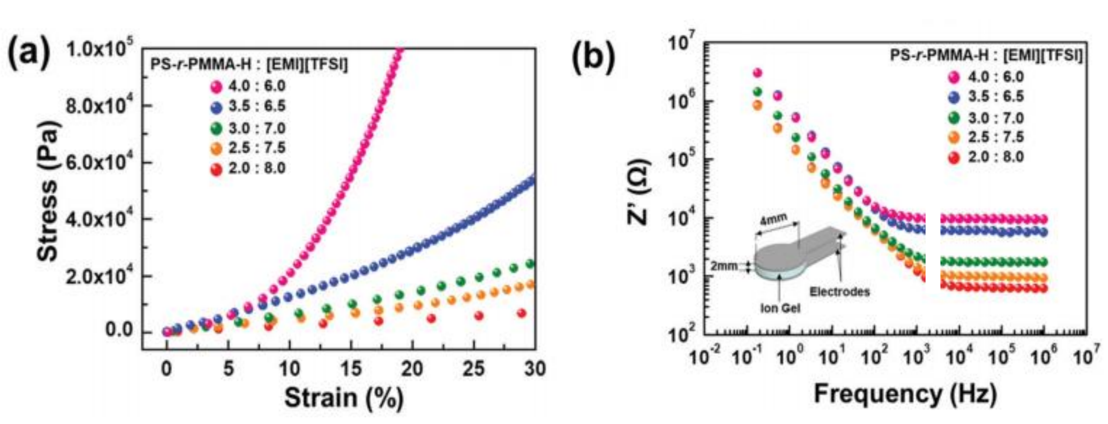


Figure 2. (a) Stress–strain curves, and (b) frequency dependence of resistance (Z') for ion gels with five different weight ratios

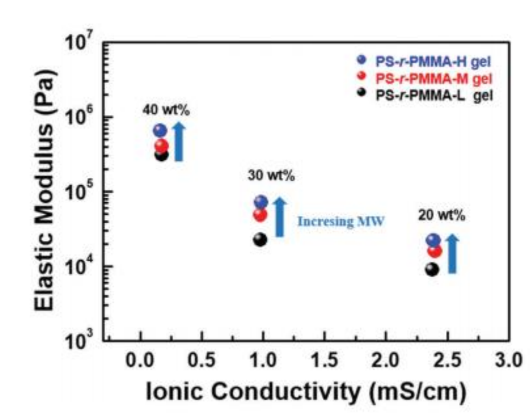


Figure 3. the effects of the molecular weight on the elastic modulus and ionic conductivity

- Elastic modulus increased and Ionic conductivity decreased when the ratio of PS-r-PMMA-H to [EMI][TFSI] increased. They are in trade-off relationship.
- The optimal condition is ion gels composed of a ratio of 3:7, with ionic conductivity ($\sim 0.98 mS/cm$) and elastic modulus ($\sim 7.2 \times 10^4 Pa$). It shows relatively high ionic conductivity than others.
- Mechanical property increased with increment of molecular weight. But A similar level of ion conductivity is measured.

(MS)6 vs. (SMS) with [EMI][TFSI]

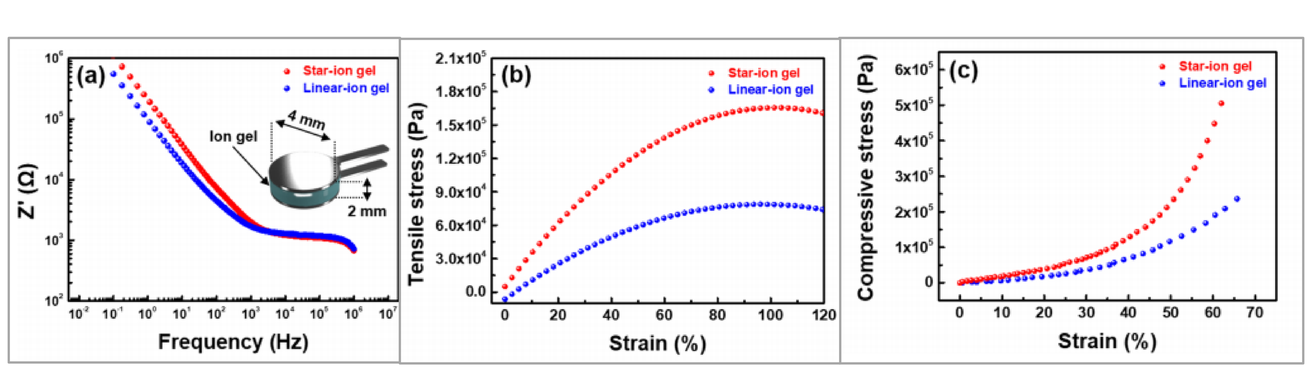


Figure 4. (a) Plots of resistance (Z') versus frequency and (b) tensile and (c) compressive stress−strain curves

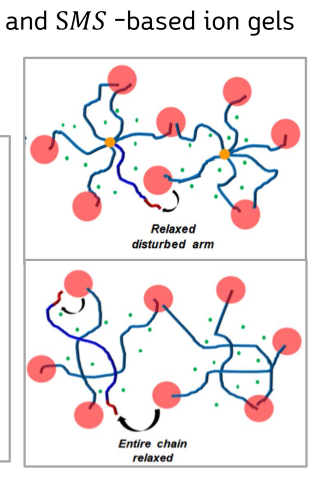


Figure 5. Schematic illustration of chain pullout under deformation for $(MS)_6$ and SMS -based ion gels

- Ionic conductivity of $(MS)_6$ and (SMS) is similar while tensile stress and compression stress are quite different.
- Star-shaped ion gel $(MS)_6$ has greater mechanical property, so good electrolyte than (SMS).

Fabrication of the e-WO_3 solid-state supercapacitors.

- The electrolyte for the solid-state supercapacitors was prepared by the following process: H_2SO_4(6 g) was mixed with deionized water (60 mL) followed by the addition of PVA (6 g, molecular weight: 100 000).

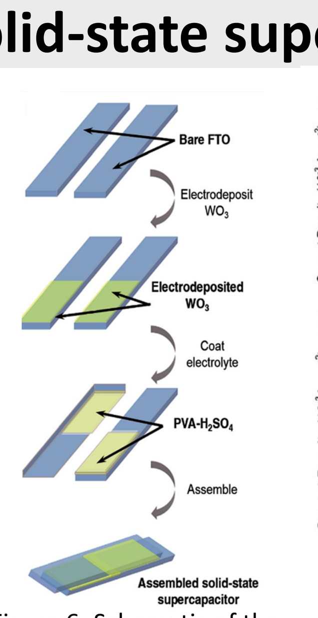


Figure 6. Schematic of the process for the fabrication of the e-WO3 solid-state supercapacitors.

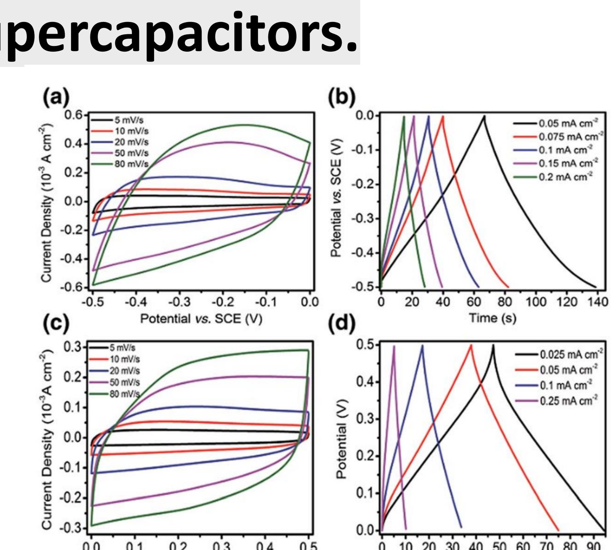
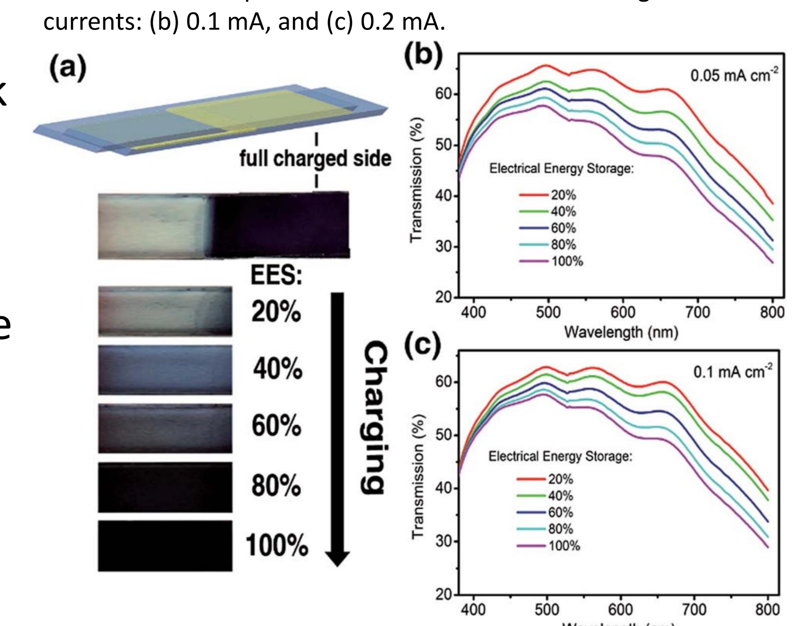


Figure 7. (a) CV and (b) galvanostatic curves of e-WO3 in 0.5 M H2SO4 electrolyte, and (c) CV and (d) galvanostatic curves of e-WO3 in the solid-state supercapacitors.

Photographs of the e-WO_3 electrode at different EESs

- Accompanying the energy storage following the reaction: $WO_3 + xH^+ + xe^- \rightarrow H_xWO_3$, the electrode will change from transparent to dark blue due to the increasing formation of blue color center W^{5+} polarons.
- Photos in Fig. 8a show the color of the electrodes at different EESs, which certifies the color change as expected.
- The electrode at the pristine state (EES= 0%) is almost transparent. During the charging process, the color becomes darker and darker with the EES increasing from 0% to 100%. A fully charged (EES = 100%) supercapacitor exhibits a dark blue appearance due to the heavy formation of W^{5+}.
- The EES can be easily estimated by identifying the color of the electrodes.

Figure 8. Photographs of the e-WO3 electrode at different EESs, and the transmission spectra of the e-WO3 electrode charged at different currents: (b) 0.1 mA, and (c) 0.2 mA.



Optical densities at 625 nm versus EES at charging/discharging currents

- Normalized optical densities at 625 nm versus the corresponding EESs are plotted in Fig. 9a and b. Accordingly, a linear dependence is clearly revealed This indicates a perfect linear dependence in spite of the charging/discharging currents.
- By using these fitted curves, we can use the normalized optical density to reveal the EES of the supercapacitors.

$$\log(T_0/T_{EES}) = \eta * EES * Q_t$$

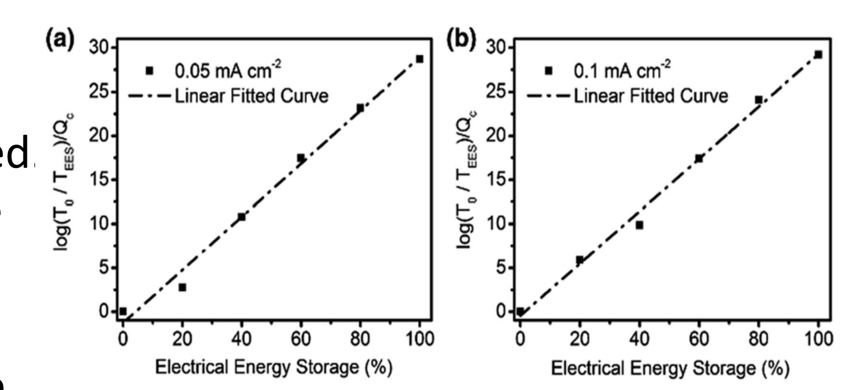
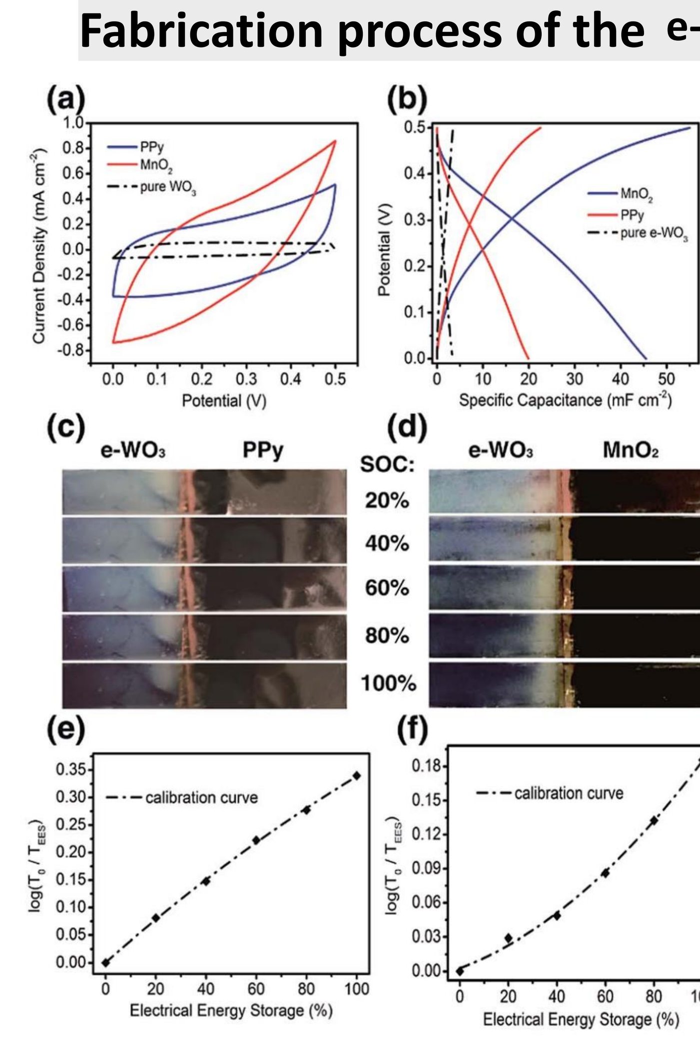


Figure 9. Optical densities at 625 nm versus EES at charging/discharging currents of 0.1 mA (a) and 0.2 mA (b), respectively. A linear dependence is clearly revealed.

Fabrication process of the e-WO_3 based hybrid solid-state supercapacitors



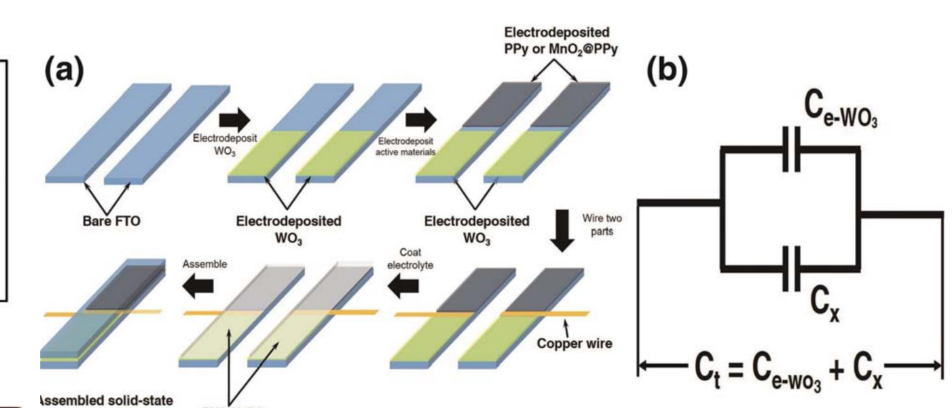


Figure 10. (a) Schematic illustration of the fabrication process of the eWO3 based hybrid solid-state supercapacitors, and (b) the equivalent circuit for the fabricated hybrid supercapacitors.

- As shown in Fig. 11b, the e-WO3//MnO2 hybrid supercapacitor possesses a capacitance of 45 mF /cm2 , which is much higher than that of the pure e-WO3 based supercapacitor.
- Also, this impressive capacitance achieved by hybrid supercapacitors is much larger than that of other electrochromic supercapacitors without the hybrid design.

$$\log(T_0/T_{EES}) = \eta * f(EES) * Q_w$$

Figure 11. (a) CV curves of the e-WO3//PPy and e-WO3//MnO2 based hybrid supercapacitors at 20 mV/s ; (b) galvanostatic charging/discharging curves of the e-WO3//PPy and e-WO3//MnO2 based hybrid supercapacitors measured at a current density of 1 mA /cm2 ; photos of the electrodes of the e-WO3//PPy hybrid supercapacitors at different EESs (c) and e-WO3//MnO2 hybrid supercapacitors at different EESs (d) and the optical densities at 625 nm versus EES of the e-WO3//PPy hybrid supercapacitors (e) and the e-WO3//MnO2 hybrid supercapacitors (f), which can be considered as a unique calibration curve solely produced for each type of hybrid supercapacitor.

Conclusion

- In ion gel electrolyte, elastic modulus and ionic conductivity is in trade-off relationship.
- The most frequently reported gel electrolytes are based on polymer-salt-solvent systems, comprising polymer like PMMA, PVC, PVA, PEO. Among them, PMMA based electrolyte have attracted in ECDs due to high transparency, solubility, and ionic conductivity. It can reach up to 4.8ms/cm of ionic conductivity.
- A visualized indicator was developed for supercapacitor devices by using e-WO3 as an active material. The color change of the electrode can be used to estimate the potential and EES of the supercapacitor.
- The normalized optical densities were found to linearly depend on the EES of the e-WO3 based supercapacitor. This founding makes it possible to quantitatively determine the EES of the supercapacitor using a simple optical transmission test.
- Hybrid supercapacitors with a parallel structure were developed in order to integrate the color-change EES indicator for high performance supercapacitors.
- By applying PMMA-based electrolytes to ECS, we can expect higher stability and performance than conventional ECSs, and we can use EC technology in many areas, including energy storage. It is expected that applied research will be further expanded.