



## Effects of Aqueous Electrolytes in Supercapacitors

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An activated carbon-carbon nanotube (AC-CNT) composite is synthesized by using a simple chemical process, and its electrochemical performance in different aqueous electrolytes, such as  $\text{H}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{KOH}$ , is investigated. The composite exhibits different capacitive behaviors in different aqueous electrolytes, demonstrating the highest specific capacitance ( $205 \text{ Fg}^{-1}$ ) in the  $\text{H}_2\text{SO}_4$  electrolyte due to its having the highest molar ionic conductivity compared to the other two. Nyquist and Bode plots prove that the composite in the  $\text{H}_2\text{SO}_4$  electrolyte has the lowest electrochemical impedance and highest capacitive behaviors compared to the others. The composite in the  $\text{Na}_2\text{SO}_4$  electrolyte has the lowest capacitance due to the low molar ionic conductivity of the electrolyte, although it displays the best capacitance retention after 200 cycles. Selection of electrolytes, therefore, is an important factor for supercapacitor applications.

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### I. INTRODUCTION

Environmental degradation and energy crisis are on the increase due to the rising human population, and clean and renewable energy are highly required, thus leading to intensified research of electrochemical energy storage system [1, 2]. Supercapacitors are energy storage devices with very high capacity and low internal resistance, which are able to deliver energy at relatively higher rates as compared to batteries due to the mechanism of energy storage which involves a simple charge separation at the interface between the electrode and the electrolyte [3]. Electrochemical double-layer capacitors (EDLCs), also called supercapacitors, are promising devices that can be used for energy storage devices in electronics, such as hybrid electric vehicles, and have long life cycle, high power density, and no pollution potential without heavy metal by-products [4, 5]. The performance of EDLC depends on not only electrode material but also electrolyte used. Lots of researches have been

done to improve specific capacitance, power density, energy density, and life cycle by choosing of appropriate electrode material and durable electrolyte. The most commonly used electrode materials are carbon allotrope due to high durability, high specific surface area of the order of  $2500 \text{ m}^2\text{g}^{-1}$ , good electrical conductivity, high chemical stability, high abundance, and low cost [6].

As for the electrolyte, there are two types of electrolytes used in EDLCs, aqueous and organic electrolytes, and the aqueous electrolytes are more suitable than the organic electrolyte in terms of low cost, high conductivity, low internal resistance, and non-flammability [7–9]. Typically three kinds of aqueous electrolytes are used, such as  $\text{H}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{KOH}$ . They have different ionic radius, especially different hydrated radius of ions. The hydrated radius of  $\text{H}^+$  in  $\text{H}_2\text{SO}_4$  is the smallest of  $2.80 \text{ \AA}$ , and the radius of  $\text{K}^+$  in  $\text{KOH}$  is the largest of  $3.31 \text{ \AA}$  [10]. The molar ionic conductivity of each ion in the electrolytes is also different. The conductivity of  $\text{H}^+$  in  $\text{H}_2\text{SO}_4$  is the largest of  $35 \text{ mSm}^2\text{mol}^{-1}$ , and  $\text{Na}^+$  in  $\text{Na}_2\text{SO}_4$  has the lowest conductivity of  $5 \text{ mSm}^2\text{mol}^{-1}$  [11].

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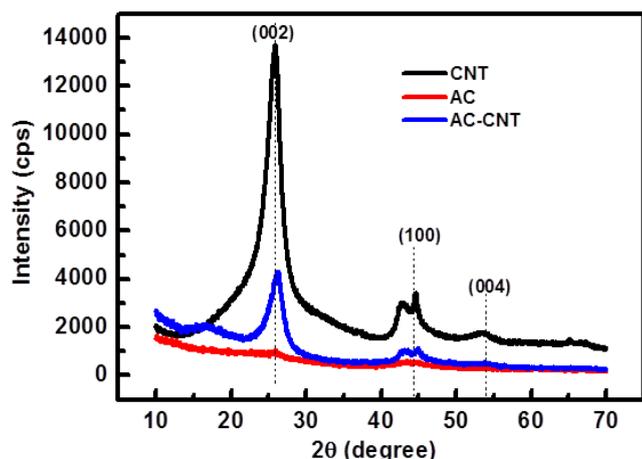


Fig. 1. (Color online) XRD of the CNT, AC, and AC-CNT sample.

In the report, three aqueous electrolytes are investigated systematically for supercapacitor application, by using cyclic voltammetry (CV), Galvanostatic charge and discharge (GCD) measurement, and electrochemical impedance spectroscopy (EIS). The electrode material of activated carbon-carbon nanotube (AC-CNT) is used because of good performance of EDLC in our previous work [12].

## II. EXPERIMENTAL

Activated carbon (AC, MSP-20, Kansai Coke and Chemicals, Japan) and Multi-walled CNT (MWCNT, CM-150, 87-93% purity, Hanwha Chemical Ltd.) were used without any pretreatment as they were. The weight of AC and CNT were measured with an analytical balance (Precisa XT220A). The ratio of AC to CNT was 2. Distilled water of 100 ml was added to the composite, and then the solution was sonicated for 2h. The sonicated solution was then filtered using a vacuum filtration method, and the filtered composite was dried in an oven for overnight. The resultant composite was turned into a powdery form by grinding. The grinded composite (AC-CNT) was used for the electrode material.

The crystalline structure of the composite was analyzed by X-ray diffraction (XRD) at 40 kV with Cu K radiation ( $\lambda = 1.54 \text{ \AA}$ ), using an automated X-ray diffractometer (D/MAX-2500/PC, Rigaku, Japan). The electrochemical properties were investigated using a three-electrode cell system with different electrolytes (1 M

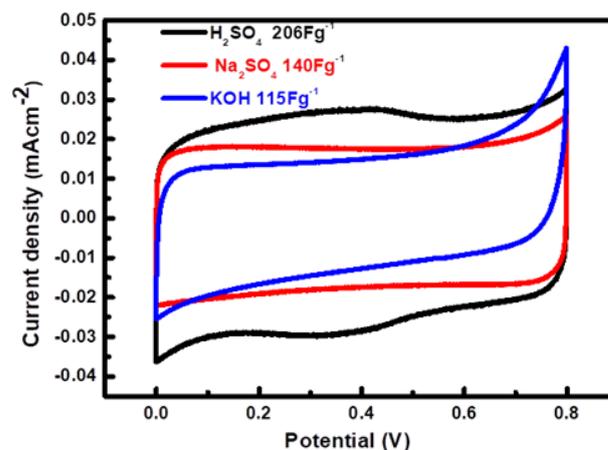


Fig. 2. (Color online) The CV results in 1 M  $\text{H}_2\text{SO}_4$ , 1 M  $\text{Na}_2\text{SO}_4$  and 1 M KOH electrolytes.

$\text{H}_2\text{SO}_4$ , 1 M  $\text{Na}_2\text{SO}_4$ , and 1 M KOH). Platinum wire was used for the counter electrode, and Ag/AgCl electrode was used as a reference electrode. 2 mg of the prepared of electrode material was sonicated with 2 ml of isopropanol for 30 mins. 5  $\mu\text{l}$  of the mixture was then dropped on glassy carbon which was then used as the working electrode. Cyclic voltammetry (CV), Galvanometric charge-discharge and EIS studies were performed using the potentiostat (SP-150, Bio-Logic, France). The potential window for the CV was 0.8 V with the scan rate of  $50 \text{ mVs}^{-1}$ , and the current density of  $5 \text{ Ag}^{-1}$  for Galvanostatic charge and discharge cycle was applied. For the EIS measurement, a frequency range of 0.01 to 500,000 Hz was used.

## III. RESULTS AND DISCUSSION

Fig. 1 shows XRD results to ensure the successful formation of the composite. No diffraction peak was observed for the AC sample because of its amorphous property, while the strongest diffraction peak was exhibited in the CNT sample at  $25.5^\circ$  corresponding to the (002) diffraction. The other characteristic diffraction peaks of CNT near  $43^\circ$  and  $53^\circ$  corresponds to (100) and (004) [13,14]. The AC-CNT composite, therefore, shows the same CNT diffraction peaks with lower intensity, indicating a successful formation of AC and CNT in the AC-CNT composite.

Fig. 2 shows the CV results in three different aqueous electrolytes. The composite in 1 M  $\text{Na}_2\text{SO}_4$  shows

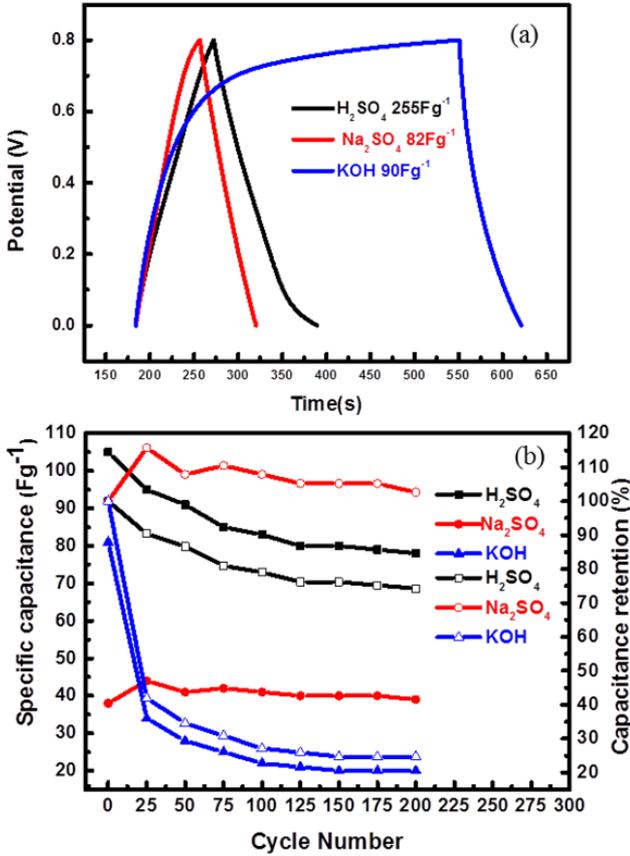


Fig. 3. (Color online) (a) The GCD results in 1 M H<sub>2</sub>SO<sub>4</sub>, 1 M Na<sub>2</sub>SO<sub>4</sub> and 1 M KOH with (b) the capacitance retention (unfilled symbols) and capacitance (filled symbols).

the characteristic EDLC of an ideal rectangular shape compared with the others. This is due to the nature of the Na<sub>2</sub>SO<sub>4</sub> electrolyte, being a neutral solution [15]. Though the current response in the 1 M KOH electrolyte was the highest at 0.8 V, it had the lowest specific capacitance of 115 Fg<sup>-1</sup>. The specific capacitance of the sample in the H<sub>2</sub>SO<sub>4</sub> electrolyte was 206 Fg<sup>-1</sup> which was the highest. The Na<sub>2</sub>SO<sub>4</sub> system showed a specific capacitance of 140 Fg<sup>-1</sup>. The differences in the specific capacitance are attributed to the hydrated ionic radius, ionic mobility, and molar ionic conductivity, and H<sub>2</sub>SO<sub>4</sub> had the lower cationic radius, higher ionic mobility and higher molar conductivity [16,17].

Galvanostatic charge-discharge curves at the current density of 5 Ag<sup>-1</sup> in the electrolytes are shown in Fig. 3(a). The charge and discharge curves of the H<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> systems are almost linear and symmetric, but a non-linear and asymmetric curve is observed in

the KOH system. The almost linear and symmetrical curve indicates good EDLC formation across the electrode/electrolyte interface while the asymmetrical curve is due to irreversible reactions between the electrode and electrolytes [18,19]. The cation of KOH has the largest radius (1.38 Å) so the charging and discharging time is longer than the others (0.02 Å for H<sup>+</sup> and 1.02 Å for Na<sup>+</sup>). The specific capacitances were calculated using the following equation.

$$C_s = \frac{I\Delta t}{m\Delta V} \quad (1)$$

where,  $I$  is the applied current,  $m$  is the mass of the active material on the electrode,  $\Delta V$  is the potential window, and  $\Delta t$  is the discharge time. The specific capacitances obtained at the current density of 5 Ag<sup>-1</sup> are about 105, 38, and 81 Fg<sup>-1</sup> for 1 M H<sub>2</sub>SO<sub>4</sub>, 1 M Na<sub>2</sub>SO<sub>4</sub> and 1 M KOH, respectively. The capacitance retention was also investigated until 200 cycles, as shown in Fig. 3(b). Left axis represents specific capacitance with filled symbols, and the right axis shows the capacitance retention with empty symbols. The absolute specific capacitance is the largest in H<sub>2</sub>SO<sub>4</sub> through 200 cycles, while the Na<sub>2</sub>SO<sub>4</sub> system shows the best capacitance retention even though it has the small specific capacitance. The KOH system shows the worst capacitance retention probably due to the high radius of the cation and irreversibility of the charge and discharge curves.

The EIS results give an insight about the restrictions of ions in pore networks of electrode materials [20]. Fig. 4(a) represents the Nyquist plot of the electrolyte systems with the inset in the mid frequency region. Deviations from vertical lines show the inner mesopore diffusion [21]. The H<sub>2</sub>SO<sub>4</sub> system showed a nearly vertical Nyquist plot with the lowest impedance with a good capacitive behavior compared to the others. The inset also shows more vertical curve of the H<sub>2</sub>SO<sub>4</sub> system compared to the other system, demonstrating highly capacitive behavior of the H<sub>2</sub>SO<sub>4</sub> system. The semicircles in the mid-frequency region (shown in Fig. 4(a) inset) are considered as equivalent series resistances (ESRs) between the electrode and the electrolytes [22], and the H<sub>2</sub>SO<sub>4</sub> system has the smallest semicircles while the KOH system has the largest semicircles, demonstrating that the H<sub>2</sub>SO<sub>4</sub> system has the lowest ESR compared to the other systems. Fig. 4(b) shows the Bode plot, phase angle versus

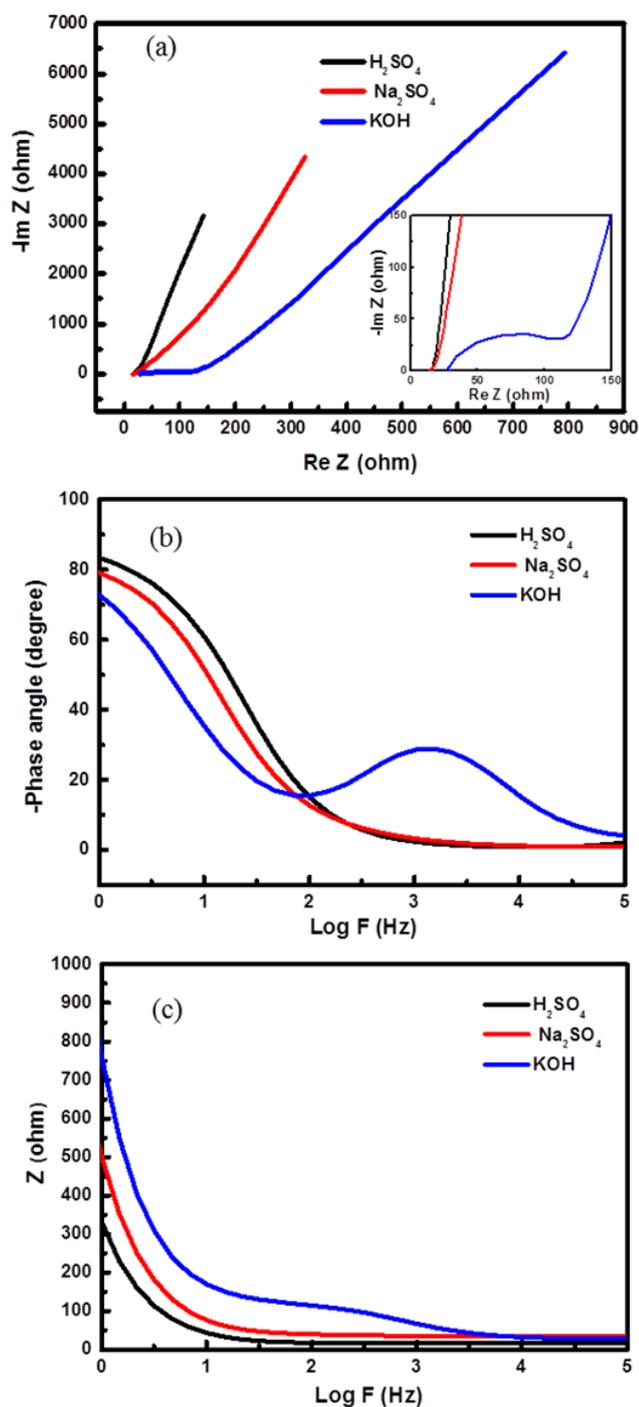


Fig. 4. (Color online) (a) Nyquist plots, (b) Bode plots, and (c) absolute impedance as a function of frequency.

log frequency, of the systems. The phase angles at  $y$ -intercept are  $-83.4^\circ$ ,  $-79.2^\circ$  and  $-72.9^\circ$  for the  $\text{H}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{KOH}$  system, respectively. The phase angles demonstrate that the  $\text{H}_2\text{SO}_4$  system is the closest to  $-90^\circ$  of the ideal capacitor, and the  $\text{KOH}$  system is the most far from the ideal capacitor. Fig. 4(c) shows

absolute impedance of the systems as a function of frequency. It is evident that the  $\text{H}_2\text{SO}_4$  system had the lowest impedance in the all frequency region, implying the best electrochemical capacitive performance, consistent with the CV and Galvanostatic charge and discharge results.

#### IV. CONCLUSION

Electrochemical performance in three different aqueous electrolytes was investigated systematically with the AC-CNT electrode material. The results reveal that the  $\text{H}_2\text{SO}_4$  system showed the best electrochemical performance in which the highest specific capacitance of  $205 \text{ Fg}^{-1}$  at the scan rate of  $50 \text{ mVs}^{-1}$ . It attributed to the smallest ionic radius, smallest hydrated radius, highest mobility, and highest molar ionic conductivity, leading to lowest electrochemical impedance and highest capacitive behavior of the  $\text{H}_2\text{SO}_4$  system. The  $\text{Na}_2\text{SO}_4$  system has lower specific capacitance than that of the  $\text{H}_2\text{SO}_4$  system, but it shows the highest capacitive retention after 200 cycles, demonstrating high cycle stability even though the specific capacitance was still lower than that 1 M  $\text{H}_2\text{SO}_4$  after 200 cycles. The  $\text{KOH}$  system showed the lowest capacitance, asymmetric charge and discharge curves, and the highest electrochemical impedance due to the largest size of the cation radius with low molar ionic conductivity. This study shows that not only the electrode material is important for building supercapacitors, but good choice of electrolytes also play a vital role in the development of supercapacitors.

#### REFERENCES

- [1] L. Dai, D. W. Chang, J. B. Baek and W. Lu, *Small* **8**, 1130 (2012).
- [2] M. K. Debe, *Nature* **486**, 43 (2012).
- [3] H. P. Wu, D. W. He, Y. S. Wang, M. Fu and Z. L. Liu *et al.*, in *2010 8th International Vacuum Electron Sources Conference and Nanocarbon* (Nanjing, China, IEEE, 2010), p. 465.
- [4] F. Jaouen, E. Proietti, M. Lefevre, J. P. Dodelet and G. Wu *et al.*, *Energy Environ. Sci.* **4**, 114 (2011).

- [5] B. Dunn, H. Kamath and J. M. Tarascon, *Science* **334**, 928 (2011).
- [6] D. W. Wang, F. Li, M. Liu, G. Q. Lu and H. M. Cheng, *Angew. Chem Int. Ed.* **47**, 373 (2008).
- [7] M. Kim, I. Oh and J. Kim, *Phys. Chem. Chem. Phys.* **17**, 16367 (2015).
- [8] G. Lota, F. Fic and E. Frackowiak, *Energy Environ. Sci.* **4**, 1592 (2011).
- [9] X. Zhang, X. Wang, L. Jiang, H. Wu and C. Wu *et al.*, *J. Power Sources* **216**, 290 (2011).
- [10] E. R. Nightingale Jr., *J. Phys. Chem.* **63**, 1381 (1959).
- [11] R. D. Shannon, *Acta Cryst. A* **32**, 751 (1976).
- [12] I. Olaniyan and H. K. Jeong, *New Phys.: Sae Mulli* **68**, 185 (2018).
- [13] T. A. Saleh, *Appl. Surf. Sci.* **257**, 7746 (2011).
- [14] C. Lu, F. Su and S. Hu, *Appl. Surf. Sci.* **254**, 7035 (2008).
- [15] L. Demarconnay, E. Raymundo-Pinero and F. Beguin, *Electrochem. Comm.* **12**, 1275 (2010).
- [16] S. Ghosh, T. Mathews, B. Gupta, A. Das and N. G. Krishna *et al.*, *Nano-structures & Nano-objects* **10**, 42 (2017).
- [17] R. S. Berry, S. A. Rice and J. Ross, *Physical Chemistry* (1980), Vol. 2, pp. 3-10 .
- [18] I. Y. Jang, H. Muramatsu, K. C. Park, Y. J. Kim and M. Endo, *Electrochem. Commun.* **11**, 719 (2009).
- [19] A. N. Naveen and S. Selladurai, *Electrochim. Acta* **125**, 404 (2014).
- [20] Y. Gochi-Ponce, G. Alonso-Nunez and N. Alonso-Vante, *Electrochem. Commun.* **8**, 1487 (2006).
- [21] W. Sugimoto, H. Iwata, K. Yokoshima, Y. Murakami and Y. Takasu, *J. Phys. Chem. B* **109**, 7330 (2005).
- [22] S. R. Sivakkumar, W. J. Kim, J. A. Choi, D. R. MacFarlane and M. Forsyth *et al.*, *Power Sources* **171**, 1062 (2007).