

Effect of Electrolyte on the Supercapacitor Behaviour of CuO Nanostructures

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Abstract

Supercapacitors, as a new class of energy storage devices, are specialised form of capacitors with an exceedingly high level of capacitance. They have received significant attention in recent years because they can achieve higher energy density than conventional capacitors and offer better power performance than batteries. The electrochemical and physical properties of the electrolytes are the key factors in determining the Equivalent Series Resistance (ESR) and the power output of a supercapacitor. In the present work, we present the effect of different electrolytes (KOH and K₂SO₄) in determining the performance of a supercapacitor based on nanostructured copper oxide (CuO) electrodes with focus on the energy storage capability. Cyclic voltammetric analysis reveals a specific capacitance of 375 Fg⁻¹ and 345 Fg⁻¹ respectively in 2 M KOH and 0.5 M K₂SO₄ at 2 mV s⁻¹.

Keywords: Supercapacitors, electrolytes, energy storage, nanostructures, CuO electrode

1.1 Introduction

An electrolyte is a critical part that governs the overall performance of a supercapacitor. The fundamental purpose of the electrolyte in a supercapacitor is to transfer ions between electrodes during charge and discharge cycles with minimal transport impedances. The type of electrolyte employed in SCs has a marked

effect on the amount of energy stored in the cell and how quickly it has released. Since both energy density and power density of a supercapacitor depend on the square of the cell voltage, a large potential stability window of the electrolyte is quite important. High electrochemical stability, wide voltage window, high ionic concentration, low ionic radius, low resistivity, high purity, low cost are the required parameters for a quality electrolyte [1].

Therefore, finding a more suitable electrolyte to optimize the performance of supercapacitors is of great significance[2]. The three primary classes of electrolytes are aqueous electrolyte, organic electrolyte and ionic liquids.

Aqueous electrolytes such as H₂SO₄, KOH, Na₂SO₄, NH₄Cl, etc., [3 – 5] possess higher ionic concentration with smaller ionic radius and lower resistance, resulting higher capacitance. They tend to produce faster rates of charge/discharge due to the relatively high conductivity and low viscosity of concentrated solutions [6]. Relatively concentrated electrolytes are required to minimize the ESR and maximize the power output [7]. Organic electrolytes are providing a voltage window as high as 3 V and ultimately an increase in energy density can be realized. Water and oxygen free atmosphere is preferred for organic electrolytes to curb the evolution of H₂ and O₂ gases since they can be operated at higher voltage

[8]. Commonly applied salts in organic electrolytes are quaternary ammonium salts out of which tetraethyl ammonium tetrafluoroborate (TEA-BF₄) is the most widely used salt for commercial supercapacitors. Salts like EMIM-BF₄ (1-ethyl-3-methylimidazolium tetra fluoroborate) or MEPY-BF₄ (1-ethyl- 1-methyl pyrrolidinium tetra fluoroborate) are currently unsuitable for industrial applications due their high cost. Instead, it is possible to use TEMA-BF₄ (triethylmethylammoniumtetrafluoroborate) at higher concentrations (2M) yielding higher ionic conductivities and avoiding ion depletion during charging of large cells at high power [9 – 10]. A major disadvantage of organic electrolytes is higher ESR due to lower conductivity and higher viscosity. Increase in viscosity, resulted in reduced wettability, which further increase the ESR and lower the capacitance [11 – 12].

Ionic Liquids (ILs) are molten salts with melting temperatures at or below room temperature, which are entirely composed of cations and anions [13]. The most studied ILs for supercapacitor electrolytes are imidazolium, pyrrolidinium, tetrafluoroborate, trifluoromethanesulfonate etc. [14]. ILs show promising properties such as high thermal stability (as high as 300°C) non-flammability with very low toxicity, non-corrosive at elevated temperatures and high electrochemical stability over a wide voltage window from 2 to 6 V [15]. However, they still cannot satisfy the requirements for large-scale supercapacitor applications due to their high price and relatively low conductivity at room temperature. The typical ionic conductivity is in the range of ~14 mS cm⁻¹ at room temperature [16]. Furthermore, maintaining the required high purity during the production requires complex processes.

In this study, aqueous electrolytes are used due to their low cost, good conductivity and safety. Two different electrolytes, 0.5M K₂SO₄ and 2M KOH were used and their effect on the energy storage capacity has been studied and reported.

2. Experimental section

2.1 Reagents and chemicals

Analytical grade copper nitrate (Cu (NO₃)₂·3H₂O), disodium citrate (Na₂H₂C₆H₅O₇), sodium hydroxide (NaOH) and ethylene glycol were purchased from Sigma Alrich, India and were utilized as such without further purification.

2.2 Synthesis of CuO nanostructures

The typical synthesis of CuO nanostructures has been reported earlier by R.Suresh et al. [17] and the same was adopted in this study.

2.3 Characterization of CuO nanostructures

Cyclic voltammetry (CV) analysis were performed using CHI 660 D electrochemical workstation (CH Instruments).

3. Results and discussion

3.1 Cyclic Voltammetric analysis

To evaluate the electrochemical performance of the CuO nanostructures, the cyclic voltammetry analysis (CV) has been carried out between -0.6 to 0.6 V using 0.5M K₂SO₄ and 2M KOH as electrolytes.

A specific capacitance of 375 Fg⁻¹ was obtained in 2 M KOH at 2 mV s⁻¹ whereas, the CuO electrode exhibits a specific capacitance of 345 Fg⁻¹ in 0.5 M K₂SO₄ electrolyte at 2 mV s⁻¹.

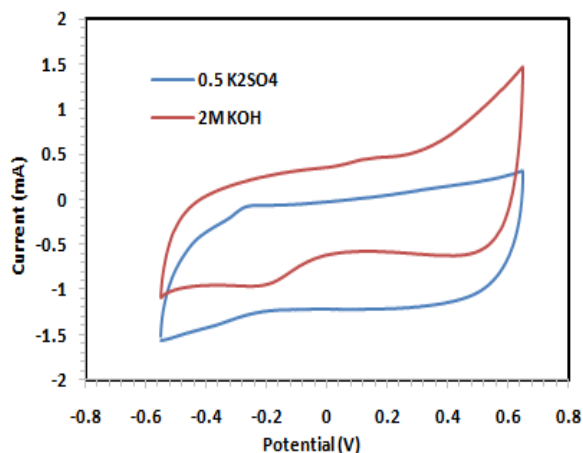


Figure 1 Cyclic voltammograms of CuO electrode in K_2SO_4 and KOH electrolytes

It is obvious from the CV curve (Fig. 1) that the presence of sharp redox peak for KOH electrolyte indicates a substantial share of pseudocapacitance.

4. Conclusion

Based on the cyclic voltammetry measurements, a maximum specific capacitance of 375 Fg^{-1} is observed for CuO based electrode in KOH electrolyte when compared to 0.5 M K_2SO_4 electrolyte. Moreover, the electrical conductivity and ion mobility of KOH electrolyte is better than K_2SO_4 substantiating its suitability as better electrolytes for supercapacitor applications.

5. References

- [1] J.K Chang, M.T Lee, W.T Tsai, M.J Deng, H.F Cheng, and I.W Sun, 'Pseudocapacitive Mechanism of Manganese Oxide in 1-Ethyl-3-methylimidazolium Thiocyanate Ionic Liquid Electrolyte Studied Using X-ray Photoelectron Spectroscopy', *Langmuir*, vol. 25, no. 19, 2009, pp. 11955-11960.
- [2] E. Frackowiak, 'Supercapacitors based on carbon materials and ionic liquids', *Journal of the Brazilian Chemical Society*, vol. 17, no. 6, 2006, pp. 1074-1077.
- [3] D. Hulicova, J. Yamashita, Y. Soneda, H. Hatori, and M. Kodama, 'Supercapacitors Prepared from Melamine-Based Carbon', *Chemistry of Materials*, vol. 17, no. 5, 2005, pp. 1241-1247.
- [4] H.Y. Lee, and J.B. Goodenough, 'Ideal Supercapacitor Behavior of Amorphous $V_2O_5 \cdot nH_2O$ in Potassium Chloride (KCl) Aqueous Solution', *Journal of Solid State Chemistry*, vol. 148, no. 1, 1999, pp. 81-84.
- [5] Zhang, Y, Feng, H, Wu, X, Wang, L, Zhang, A, Xia, T, Dong, H, Li, X & Zhang, L, 'Progress of electrochemical capacitor electrode materials: A review', *International Journal of Hydrogen Energy*, vol. 34, no. 11, 2009, pp. 4889-4899.
- [6] Fletcher, SL, Sillars, FB, Hudson, NE & Hall, PJ, 'Physical Properties of Selected Ionic Liquids for Use as Electrolytes and Other Industrial Applications', *Journal of Chemical and Engineering Data*, vol. 55, no. 2, 2010, pp. 778-782.
- [7] B.E. Conway, *Electrochemical Supercapacitors: Scientific fundamentals and Technological Applications*, Kluwer Academic Publishers/Plenum Press, New York, 1999.
- [8] R. Kotz, and M. Carlen, 'Principles and applications of electrochemical capacitors', *Electrochimica Acta*, vol. 45, no. 15-16, 2000, pp. 2483-2498.

- [9] K. Mori Ida and M. Ue, 'Process for Producing Quaternary Salts', European Patent Office, EP 0291074, 1988.
- [10] M. Ue, M. Takehara, and M. Takeda, 'TriethylmethylammoniumTetrafluoroborate as a highly soluble supporting electrolyte salt for electrochemical capacitors', *Denki Kagaku Electrochemistry*, vol. 65, no. 11, 1997, pp. 969-971.
- [11] M. Arulepp, L. Permann, J. Leis, A. Perkson, K. Rumma, A. Janes, and E. Lust, 'Influence of the solvent properties on the characteristics of a double layer capacitor', *Journal of Power Sources*, vol. 133, no. 2, 2004, pp. 320-328.
- [12] P. Liu, M. Verbrugge, and S. Soukiazian, 'Influence of temperature and electrolyte on the performance of activated-carbon supercapacitors', *Journal of Power Sources*, vol. 156, no. 2, 2006, pp. 712-718.
- [13] A. Balducci, R. Dugas, P.L. Taberna, P. Simon, D. Plee, M. Mastragostino, and . Passerini, 'High temperature carbon-carbon supercapacitor using ionic liquid as electrolyte', *Journal of Power Sources*, vol. 165, no. 2, 2007, pp. 922-927.
- [14] G.P. Wang, L. Zhang, and J.J. Zhang, 'A review of electrode materials for electrochemical supercapacitors', *Chemical Society Reviews*, vol. 41, no. 2, 2012, pp. 797-828.
- [15] A. Burke, R&D considerations for the performance and application of electrochemical capacitors, *ElectrochimicaActa*, vol. 53, no. 3, 2007, pp. 1083-1091.
- [16] M. Galinski, A. Lewandowski, and I. Sępnia, 'Ionic liquids as electrolytes', *ElectrochimicaActa*, vol. 51, no. 26, 2006, pp. 5567-5580.
- [17] R. Suresh, K.Tamilarasan, and D.Senthil Vadivu, "Synthesis and characterization of copper oxide nanostructures for supercapacitor electrode applications", *Journal of Ovonic Research*, Vol. 12, No. 4, 2016, pp. 215 – 223.