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COMMUNICATION

Contact Angle Measurement: A Preliminary Diagnostic Tool for Evaluating the Performance of ZnFe₂O₄ Nano-flake based Supercapacitors

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Contact angle measurement (surface wettability) of the electrolytes (1M KOH, NaOH and LiOH) and their combination (1M 1:1 v/v LiOH+KOH, NaOH+KOH and LiOH+NaOH) in contact with ZnFe₂O₄ nano-flake based electrodes is used as an empirical diagnostic tool to pre-evaluate the performance of supercapacitor prior to actual fabrication of the device.

Supercapacitors have recently gained tremendous popularity as a low-cost alternative to electrical energy storage for portable electronic devices.^{1,2} The operating principle of supercapacitor is charge accumulation on electrode-electrolyte interface (Electric double layer capacitors)^{3,4} or Faradic redox reaction (Pseudocapacitors).^{5,6} Metal oxides (binary or tertiary) are among the most explored electrode materials including the ferrites.⁷ Among the ferrites, ZnFe₂O₄ is one of promising candidate for its interesting properties like fast electron mobility, multiple oxidation state of iron for fast charging and discharging, low cost, abundance, non toxicity and is also environmentally benign.⁸⁻¹¹ Furthermore, ZnFe₂O₄ have tunable morphologies such as nanorods,⁸ microspheres,⁹ nanocubes¹⁰ and nano-flakes,¹¹ which govern its electronic properties rendering this a versatile material. Moreover, such different morphologies were also explored in supercapacitor applications in conjunction with aqueous¹² and organic electrolytes (ionic liquids)¹³ to achieve higher specific capacitance and energy density. The electrode material, electrolyte, large surface area at the ZnFe₂O₄/electrolyte interface, intercalation and de-intercalation of the electrolytic ions and high charge storage density is a prerequisite and plays an important role in efficient storage of energy.^{14,15} Thus, choice of appropriate electrode material and electrolyte

combination is yet a challenge pursued to achieve optimum supercapacitor performance.¹⁶ Therefore, in order to achieve and optimize the output performance, one requires extensive work and repeated experiments to be performed while developing supercapacitor systems.^{17,18} However, fabricating a supercapacitor device and to evaluate its performance is a tedious, time consuming and laborious process. Thus, there is a need to develop a simple method, which could be correlated with the performance. This would help one to get a rough prior estimate of supercapacitive performance before fabricating the actual device.

Surface wettability test which involves the interaction between a liquid and a solid in contact, is an important parameter in surface science and its measurement provides a simple and reliable technique for the interpretation of surface engineering.¹⁹ With this motivation, in the present work, we have developed a simple and economic approach by establishing an empirical diagnostic relationship between contact angle (CA) measurement (surface wettability) and energy storage efficiency for mechanochemically deposited ZnFe₂O₄ nano-flake thin films using 1M (KOH, NaOH, LiOH and their combination mixtures 1 M 1:1 v/v of each electrolyte LiOH+KOH, NaOH+KOH, LiOH+NaOH) electrolytes with unified concentration. The CA calibrated using Young's equation (sessile drop method) on the ZnFe₂O₄ nano-flake surface is measured for different electrolytes in contact.²⁰ This is an economical and environmentally acceptable approach that minimizes the time taken, reduces use of chemicals, money, sophisticated instrumentation requirements and labour, if evaluation (CA measurement) is performed prior to actual device fabrication, thereby addressing the green chemistry principles. This method could serve as a diagnostic technique to evaluate the quality or performance of ZnFe₂O₄ nano-flakes based supercapacitor without actually fabricating the supercapacitor device and is reported for the first time.

The conducting stainless steel (SS) substrates were cleaned prior to mechanochemical deposition of ZnFe₂O₄ nano-flakes as reported earlier.¹¹ In typical experiments, the SS substrate immersed in an aqueous solution of zinc chloride (0.1 M,

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Merck) and iron (II) chloride (0.2 M, Merck) maintained at 55 °C was rotated at 55 rpm and the deposition was carried out for 3h. The SS substrates after completion of deposition were then annealed at 550 °C for 5h in a closed furnace under ambient air atmosphere and subsequently allowed to cool down naturally in the same atmosphere. Same structure ZnFe₂O₄ nano-flake electrodes (prepared in same batch) were used for the experiments for better comparison of the trends.

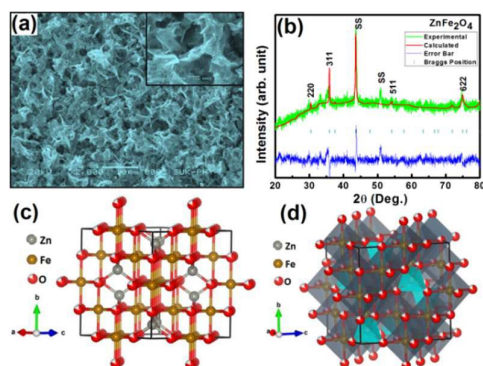


Fig. 1 Representative a) SEM image and b) XRD pattern obtained from ZnFe₂O₄ nano-flakes thin films (inset is SEM at higher magnification) (c) Side view and (d) Polyhedral crystal structure of ZnFe₂O₄ in thin film form.

Fig. 1(a) is a representative SEM image (JSM-6360 JEOL; SEM) obtained from the ZnFe₂O₄/SS electrode. The SEM images clearly show network of ZnFe₂O₄ nano-flakes grown upright against the SS substrate surface and are uniformly distributed over the surface with void length of ~500 nm-1µm. Inset (right top) in Fig. 1(a) shows the high resolution image of ZnFe₂O₄/SS electrode demonstrating the average flake size of about ~25 nm.¹¹ Fig. 1(b) shows the XRD pattern (XRD; Philips Japan MPD 1880 using Cu Kα₁ radiation) in the 2θ range of 20°-80° obtained from the ZnFe₂O₄/SS electrode with a scan rate of 4° min⁻¹. The resulting XRD pattern is also well fitted by Rietveld fitting analysis with space group Fd3̄m as shown in Fig. 1(b).²¹ The XRD pattern clearly shows the dominance of the (311) over the (220) peak, suggesting the formation of ZnFe₂O₄ cubic spinel nano-network. The peak intensity of the (311) plane in the XRD pattern is sensitive to the concentration of oxygen vacancies. The higher the number of oxygen vacancies, the lower is the resistivity, and therefore, the best conducting electrodes should ideally have a zero peak intensity for the (311) peak. The presence of the (311) peak with relatively lower intensity indicates that, the mechanochemically deposited ZnFe₂O₄/SS electrodes can be used as an active working electrode in supercapacitors. The peaks marked with SS correspond to those of stainless steel reflections. The arrangement of atoms in their crystal structure were confirmed by models as shown in Figs. 1(c) and 1(d), which clearly indicate that the synthesized ZnFe₂O₄ thin films are of spinel face centered cubic (FCC) crystal structure.²²

The shape of liquid drops in the presence of gravity can be described by Laplace's equation, which relates surface tension of the liquid to the pressure difference across the liquid/air

interface.²³ Fig. 2 shows the CA (Surface Electro-Optics, Model-Phoenix 150 CA analyzer) photographs of different electrolytes in contact with the bare ZnFe₂O₄/SS electrode, which demonstrates the extent of permitted intercalation of electrolytic ions, their corresponding specific capacitance and viscosity (measured using Ostwald viscometer). The presence of porous network in between the ZnFe₂O₄ nano-flakes enables the adsorption of 1M KOH liquid droplet completely within the pore space demonstrating superhydrophilicity on the surface (CA = 12°). On the other hand, CA of 1M NaOH, 1M LiOH and pure water showed increasing trend of CA viz. 35°, 140° and 147°, respectively. Similarly, the combined mixture of electrolytes LiOH+KOH (47°), NaOH+KOH (68°) and LiOH+NaOH (122°) also showed increasing trend of CA. This indicates that the adsorption of K⁺ ions of KOH electrolytes leads to formation of smaller hydrated ions, which enhances the intercalation of ions within the pores of ZnFe₂O₄ nano-networks, unlike NaOH and LiOH (forming larger hydrated ions thereby limiting intercalation).²⁴ This is attributed to the change in surface-interface properties of ZnFe₂O₄ network in the presence of different aqueous electrolytes.

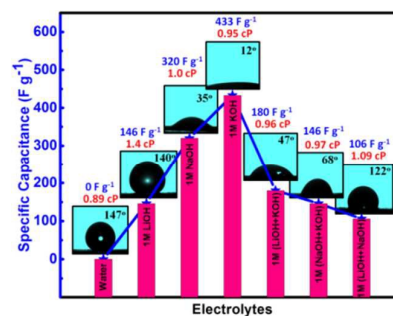


Fig. 2 Correlative study of contact angle measurement (CA), viscosity (cP) and Specific capacitance (F g⁻¹) of ZnFe₂O₄ thin films using different aqueous electrolytes (1 M) and their mixture combination (1 M 1:1 v/v each electrolyte).

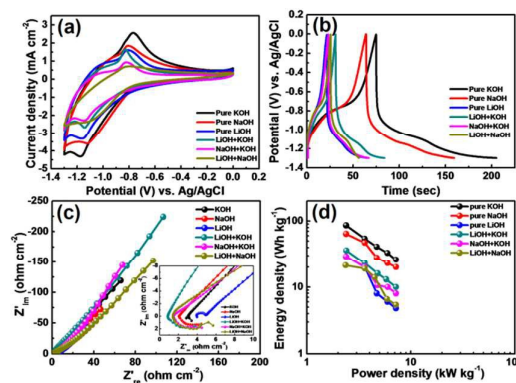


Fig. 3 a) Cyclic voltammograms (CV) at 10 mV s⁻¹ scan rate b) Charge-discharge curves at 2 mA cm⁻² current density c) Nyquist plots and d) Ragone plot of ZnFe₂O₄ nano-flakes thin films using different aqueous electrolytes (1 M) and their mixture combination (1 M 1:1 v/v each electrolyte).

The electrochemical properties (CHI608 electrochemical analyzer) were studied using three electrodes system. Fig. 3(a)

shows the cyclic voltammograms (CV) of ZnFe₂O₄ nano-flake electrode with individual 1M KOH, NaOH, LiOH and their mixture combination LiOH+KOH, NaOH+KOH and LiOH+NaOH (1M 1:1v/v of each electrolyte). All the CV curves exhibited pair of redox peaks within the potential window (0.0 to -1.3 V) indicating the fact that ZnFe₂O₄ nano-flake thin films shows pseudocapacitive behaviour in aqueous electrolytes or their mixtures. Furthermore, the larger area under the CV curves for 1M KOH electrolyte indicates the fast intercalation and de-intercalation of small hydrated K⁺ ion within the open pores of the nano-flakes network and thus high specific capacitance. This is in good agreement with the smaller CA value of 12° (hydrophilic) and larger surface energy (SE) of 71 mJ m⁻².

The area under the curves for 1M NaOH and 1M LiOH showed decreasing trend same as that observed for specific capacitance, which indicates that the size of the hydrated ions of Na⁺ and Li⁺ increases, thereby retarding the intercalation and de-intercalation events. This is further supported by the observed increasing trend of CA values of 35° (NaOH) < 140° (LiOH) trending towards hydrophobic nature and smaller surface energies (SE) 44 mJ m⁻² and 0.5 mJ m⁻², respectively, than that for 1M KOH electrolyte.

In order to find the effect of hydrated ions on specific capacitance and CA values, combined mixture of each electrolyte LiOH+KOH, NaOH+KOH and LiOH+NaOH is also studied. Fig. 3a shows CV curves obtained with combined mixture of electrolyte LiOH+KOH, NaOH+KOH and LiOH+NaOH. It is observed that the mixture of LiOH+KOH shows maximum area under the CV curve than NaOH+KOH and LiOH+NaOH electrolyte combination, which indicates that the hydrated impurity ions directly affects the performance of supercapacitors. The results were further confirmed by measuring the CA values, surface energies, conductivities (ms) and viscosities (cP) of each individual electrolyte and mixture combination and are in good agreement with the observed trends as shown in Fig. 2. For further investigation of supercapacitive properties, the galvanostatic charge-discharge (GCD) measurements were carried out in the same aqueous electrolytes and their combined mixture of electrolytes at constant current density of 2 mA cm⁻² between the potential windows 0.0 to -1.3 V as shown in Fig. 3b. From the figure, it is observed that the triangular shape of GCD curves is in good agreement with CV curves showing pseudocapacitive behaviour. The specific capacitances (F g⁻¹) were calculated using discharging curves. The calculated specific capacitance of ZnFe₂O₄ nano-flake for the electrolyte and mixture combination at the constant current density of 2 mA cm⁻² showed decreasing trend (KOH (433 F g⁻¹) > NaOH (320 F g⁻¹) > LiOH (146 F g⁻¹) and LiOH+KOH (180 F g⁻¹) > NaOH+KOH (146 F g⁻¹) > LiOH+NaOH (106 F g⁻¹)) similar to the decreasing trend of surface energies 71, 44, 0.5 mJ m⁻² and 58, 34, 18 mJ m⁻², respectively. While the CA measurements showed contrary trend of increase in CA values with decreasing specific capacitance and surface energy as shown in Fig. 2 and 3. The observed variation in mixed combination of electrolytes can be attributed to combined effect of hydrated ions and/or competition for abstraction of hydrated species.

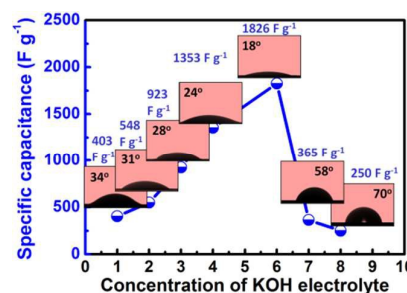


Fig. 4 Correlative study of contact angle measurement (CA) and specific capacitance (F g⁻¹) of ZnFe₂O₄ nano-flake electrodes as a function of varying concentration of KOH electrolyte.

The EIS measurement is one of the important parameter for supercapacitor application. Therefore, the Nyquists plots were recorded for ZnFe₂O₄ nano-flakes in the same aqueous electrolytes and their combination mixtures as shown in Fig. 3 (c). It shows that, electrolytes demonstrating the presence of small semicircles called as charge transfer resistance (R_{ct}) and smaller equivalent series resistance (ESR) indicate good capacitive behaviour. The R_{ct} (0.10 ohm cm⁻²) and ESR (3.4 ohm cm⁻²) values for 1M KOH electrolytes are smaller than 1M NaOH (0.20 and 4.4 ohm cm⁻²) and 1M LiOH (0.98 and 4.0 ohm cm⁻²) electrolytes, respectively. Furthermore, the R_{ct} and ESR values of LiOH+KOH, NaOH+KOH and LiOH+NaOH combined mixture of electrolytes are 0.08, 0.4, 0.8 ohm cm⁻² (R_{ct}) and 3.9, 4.5, 5.7 ohm cm⁻² (ESR), respectively. These results are also in good agreement with the observed trends for CA and SE values. This confirms the observation of ZnFe₂O₄ nano-flake thin films showing better performance in 1M KOH electrolyte compared to other used electrolytes and is in agreement with earlier literature reports.^{25,26} Fig. 3d shows Ragone plots demonstrating the energy density trend as KOH (86 Wh kg⁻¹) > NaOH (64 Wh kg⁻¹) > LiOH+KOH (36 Wh kg⁻¹) > NaOH+KOH (29.3 Wh kg⁻¹) > LiOH (29 Wh kg⁻¹) > LiOH+NaOH (21.2 Wh kg⁻¹) at power density of 2.4 kW kg⁻¹ in conjunction with specific capacitance trend, which is reverse to that observed in CA measurements. Furthermore, the study investigating the influence of concentration of KOH electrolyte on surface wettability (CA measurement) and thus the performance (specific capacitance) was performed in the concentration range of 1-8 M. The results show increasing trend of specific capacitance from 1M to 6M and beyond which decrease in specific capacitance was noted as a result of saturation. On the contrary, the CA value showed decreasing trend from 1M to 6M and beyond which increase in CA value was noted as shown in the Fig. 4 and ESI Fig. S1. Interestingly, similar correlative trend in CA (surface wettability) and specific capacitance is also observed for ZnFe₂O₄ nano-grain thin films as electrode (ESI Fig. S2 and S3) and might also be extended to electrodes of varying ZnFe₂O₄ morphologies or other electrode-electrolyte combinations. This work is underway for investigation of the same.

Conclusions

In conclusion, a simple mechanochemical approach is used to grow ZnFe₂O₄ nano-flake thin films as electrode for supercapacitor applications, which is used for preliminary evaluation and correlation of supercapacitor performance by measuring the CA (surface wettability), SE and viscosity of the electrolytes [1M LiOH, NaOH, KOH and mixture combination of electrolytes (LiOH+KOH, NaOH+KOH and LiOH+NaOH; 1:1 v/v of 1M of each electrolyte)] in contact with the electrode, prior to actual fabrication of the device. The ZnFe₂O₄ nano-flake electrode gives smaller CA value (12°) and maximum SE value (71 mJ/m²) and specific capacitance (433 F g⁻¹) at 2 mA cm⁻² current density with 1M KOH electrolyte revealing better surface wettability and supercapacitor performance. On other hand, ZnFe₂O₄ nano-flake electrode demonstrates relatively larger CA values and smaller SE values and specific capacitances for all the other electrolyte and electrolyte mixtures. Furthermore, the use of electrolyte mixtures demonstrated less specific capacitances than use of individual electrolytes. This implies that impurities in electrolyte are detrimental for electrochemical performance of supercapacitors. Good correlation and interesting trend of increasing specific capacitance and energy density is observed with decreasing CA value and viscosity of the electrolyte in contact with electrode, which forms the basis of preliminary evaluation of the supercapacitor performance of the electrode-electrolyte combination. This would save time, chemical, money, requirements of sophisticated instrumentation and labour, if evaluation is performed prior to fabrication of the device. Furthermore, surface engineering is important and governs the performance, where CA measurement would be handy tool to evaluate qualitative and quantitative information on the chemical nature of the surface and interaction of electrolyte with the electrode. The significance of the work lies in the fact that the physical property i.e. CA (surface wettability) of the electrode surface in contact with electrolyte is used for preliminary diagnosis for evaluating or estimating the performance of the supercapacitor. We believe that this observed correlative trend is of potential scientific significance.

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