

# Use of Oxide Nanofluids as Electrolytes in Sodium Ion Supercapacitor

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## Abstract

This work studies the use of novel multifunctional materials for a sodium ion supercapacitor. The multifunctional material used was nanosized perovskite oxide in combination with vanadium pentoxide ( $V_2O_5$ ), or modification of electrolyte solution of 1M  $NaClO_4$  in propylene carbonate with nanofluids of copper oxide and iron oxide in ethanol. These nano-oxides are incorporated in addition to cathode nanomaterials like multiwalled carbon nanotubes (MWCNT), sulphur, cellulose, activated carbon. It is seen that use of the nanosized perovskite oxide and vanadium pentoxide results in higher cathodic current, higher gram capacitance of 33 F/g, energy density of 125 Wh/kg, power density of 20 kW/kg and current carrying capacity of 200 mA/hg and are comparable to the best values in literature. Applications for the work is in the areas of high energy and power density sodium ion capacitors and batteries that can be used in electronics, household applications.

**Keywords:** nanofluids, electrolyte, sodium

## 1.0 Introduction

The most challenging task that is involved in developing an energy storage device is that the device has to be maintained with both high energy density as well as high power density [Paek et al 2018]. When compared to capacitors and batteries, these requirements can be partially satisfied by using supercapacitors. Basically, supercapacitors have high energy density when compared to conventional capacitors and have high power density when compared to batteries [Liu et al; 2016, Passerini et al; 2016]. Supercapacitors have high cyclic stability of about 10000-100000 cycles whereas cyclic stability of Li-ion batteries is limited to less than 1000 cycles [Chao et al; 2017].

The major drawback of lithium based devices is that they only last for about three to four years after they are manufactured [Miyamoto et al; 2012]. Due to demand for the storage device and scarcity of lithium metal in the earth crust,

the cost of lithium as well as storage devices has been increased. If the lithium based devices are completely discharged, then they cannot be recharged again and are very sensitive to high temperatures. Also, some safety issues have been reported regarding the usage of lithium batteries in the daily life [Eftekhari and Kim; 2018, Bin et al; 2017].

Therefore, it has become necessary to replace lithium with other resources for storage devices such as sodium, aluminum, carbon, magnesium etc. When compared to other materials, sodium is most abundant metal and it has high voltage potential vs. standard hydrogen electrode (SHE). For sodium ion capacitors and batteries, there are different materials that can be used as electrode materials. Different anode materials are employed such as hard carbon, carbon nanotubes, activated carbon, graphene, metallic sodium, titanium spinal and conversion materials. Cathode materials used include nanomaterials such as carbon nanotubes, activated carbon, sodium transition metal phosphates ( $Na_3V_2(PO_4)_3$ ), Prussian blue, conducting polymers and transition metal oxides which include  $MnO_2$ ,  $V_2O_5$ ,  $RuO_2$ , NiO

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etc.[Kim et al; 2015]. The intercalation and de-intercalation of sodium ions in commercially available MWCNTs and single walled carbon nanotube (SWCNTs) were studied, but the cost of SWCNT is very much higher than that of MWCNT [Vinay et al; 2016]. Different salts and solvents can be used as an electrolyte in sodium ion devices. Some of the salts include  $\text{NaClO}_4$ ,  $\text{NaPF}_6$ ,  $\text{NaBF}_6$  and  $\text{NaTFSI}$  and solvents include Ethylene carbonate (EC), Propylene Carbonate (PC), Dimethyl Carbonate (DMC), Diethyl carbonate (DEC), etc.[Kim et al; 2015, Li et al; 2016]. These electrolytes used can be a form of liquid, semi-liquid (gel) and solid state. They are called as “aqueous liquid electrolytes”, “non-aqueous electrolytes”, “ionic liquid electrolytes”, “solid polymer electrolytes” etc. For sodium batteries, aqueous electrolyte salts like  $\text{NaClO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{NaNO}_3$  are used and are inexpensive. In search of suitable salt for non-aqueous electrolyte, salts like  $\text{NaClO}_4$  and  $\text{NaPF}_6$  with different organic solvents showed good results [Li et al; 2016]. When CNT was used in combination with graphene, the results showed superior electrochemical properties, energy density, maximum power density and specific capacitance in an ionic liquid [Tang et al; 2011].  $\text{NaClO}_4$  salt showed better results when it was mixed with Propylene Carbonate. This salt also provided good results with high conductivity in organic solvent of ethylene carbonate (EC) and dimethylene carbonate (DMC) with the ratio of 1:1 being the best mixture among the different samples [Abd Azees et al; 2017]. K. Vignarooban et al. reviewed on present research work on sodium based batteries and challenges that are involved in it related to intercalation and de-intercalation of sodium ions. The reviewers also mentioned about gaining of momentum towards the development of sodium based batteries due to reasons like non-abundance of lithium in earth crust, cost and safety regarding lithium based batteries. This study also involved different types of electrolytes and selection of particular electrode materials [Vignarooban et al; 2016]. There was a lot of research on  $\text{V}_2\text{O}_5$  and was found that it was one of the most suitable electrode materials in aqueous and organic electrolytes for pseudocapacitors due to its non-artificial abundance, high energy density, low toxicity, low cost, mixed oxidation states, high capacitance and ease of fabrication.  $\text{V}_2\text{O}_5$  limits the specific capacitance improvement because its specific surface area and solubility are low. Due to its controlled morphology,  $\text{V}_2\text{O}_5$  is recommended to be a best electrode material for supercapacitor [Cook et al; 2016].

Our group have recently published [George et al; 2022] on sodium ion capacitor with high energy density of 112 Wh/kg, high power density of 12 kW/kg and specific capacitance of 14.6 F/g. In a recent review article by our group [Nikitha et al; 2022], we have reviewed different anode and cathode materials and electrolytes for sodium ion devices. This work attempts an improvement over our recent work and studies the use of novel multifunctional materials as cathode coatings

as well as electrolyte, for a sodium ion supercapacitor. The multifunctional material used was nanosized perovskite oxide in combination with vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) or modification of electrolyte solution of 1M  $\text{NaClO}_4$  in propylene carbonate with nanofluids of copper oxide and iron oxide in ethanol. These nano-oxides are incorporated in addition to cathode nanomaterials like MWCNT, sulphur, cellulose, activated carbon. It is seen that use of the nanosized perovskite oxide and copper oxide nanofluid results in higher cathodic current, higher gram capacitance of 33 F/g, energy density of 125 Wh/kg, power density of 20 kW/kg and current carrying capacity of 200 mAh/g.

## 2.0. Materials and Experimentation

Different types of materials such as  $\text{NaCl}$ , activated carbon, MWCNT, sulphur, cellulose,  $\text{Cs}_2\text{NaBiCl}_6$  and metal oxide  $\text{V}_2\text{O}_5$  was selected for electrode materials.

- Cathode electrode: For the first sample, the cathode electrode was prepared by mixing  $\text{NaCl}$  - 0.1g, MWCNT - 0.15g, activated carbon (AC) as a conductive material - 0.1g. Sulphur was selected as it enhances the current. Sulphur was used as an enhancer - 0.1g and cellulose was used as a binder to bind all the materials completely and was used in quantity - 0.15g.
- Anode electrode: The anode electrode was prepared by using MWCNT as active material - 0.09g, AC as conductive material - 0.08g, sulphur as enhancer - 0.1g and cellulose as a binder - 0.13g.
- Adding copper oxide to electrolyte solution electrolyte preparation: The electrolyte was prepared by using  $\text{NaClO}_4$  (Sodium Perchlorate), nanosized copper oxide ( $\text{CuO}$ ) as electrolyte salt and PC (propylene carbonate), ethanol was used as electrolyte solvent for copper oxide. 1M concentration of  $\text{NaClO}_4$  was prepared. The electrolyte was prepared by dissolving 1.22g of  $\text{NaClO}_4$  in 10 ml of propylene carbonate and 0.15g of copper oxide was mixed in 5 ml of ethanol. Once the salts are dissolved, both the solutions were mixed completely to form a uniform solution.
- Adding Iron oxide to the electrolyte solution electrolyte preparation: The electrolyte was prepared by using  $\text{NaClO}_4$  (sodium perchlorate), nanosized iron oxide (mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ) as electrolyte salt and PC (propylene carbonate), ethanol was used as electrolyte solvent for iron oxide. 1M concentration of  $\text{NaClO}_4$  was prepared. The electrolyte was prepared by dissolving 1.22g of  $\text{NaClO}_4$  in 10 ml of propylene carbonate and 0.15g of iron oxide was mixed in 5 ml of ethanol. Once the salts are dissolved, both the solutions were mixed completely to form a uniform solution.
- Electrochemical cell assembly: The anode and cathode

electrode is prepared as discussed in section 2a and 2b. The electrochemical testing cell was prepared by sandwiching together the anode electrode || separator || cathode electrode. All the samples are held tightly using two clips by placing them between glass strips. Entire electrochemical measurements were done at ambient temperature. The investigations were performed by using three-electrode CH instruments with CHI 608E electrochemical analyser software. This system is basically designed with Ag/AgCl as a reference electrode. The metal oxide coated conducting electrode material i.e., cathode electrode is used as a working electrode and anode electrode as a counter electrode

## 3.0 Results and Discussion

### 3.1 Electrochemical Analysis

The cyclic voltammetry (CV) analysis technique is one of the simplest and most commonly and widely used experimental technique to investigate the electrochemical behaviour of the supercapacitor. Base electrode components are NaCl, activated carbon, MWCNT, sulphur, cellulose. The CV experiments and analysis consisted of:

- base electrode components along with addition  $\text{Cs}_2\text{NaBiCl}_6$  and metal oxide  $\text{V}_2\text{O}_5$  with 1M  $\text{NaClO}_4$  in PC
- base electrode components along with addition  $\text{Cs}_2\text{NaBiCl}_6$  and metal oxide  $\text{V}_2\text{O}_5$  with 1M  $\text{NaClO}_4$  in PC and 0.15g copper oxide in 5 ml ethanol
- base electrode components with 1M  $\text{NaClO}_4$  in PC and 0.15g copper oxide in 5 ml ethanol
- base electrode components with 1M  $\text{NaClO}_4$  in PC and 0.15g Iron oxide in 5 ml ethanol
- base electrode components along with addition  $\text{Cs}_2\text{NaBiCl}_6$  and metal oxide  $\text{V}_2\text{O}_5$  with 1M  $\text{NaClO}_4$  in PC and 0.15 g iron oxide in 5 ml ethanol

The scan rate of 0.1 V/s and voltage window of -2V to 2V was used. When base electrode components along with addition  $\text{Cs}_2\text{NaBiCl}_6$  and metal oxide  $\text{V}_2\text{O}_5$  with 1M  $\text{NaClO}_4$  in PC was used, a high current of 0.18 mA was obtained (Fig.1a). Redox cycling was done for 60 cycles and found to show stable behaviour. The calculated energy density, power density, current carrying capacity were 125 Wh/kg, 20 kW/kg, 200 mAh/g from Fig 1a (refer [George et al; 2022] for standard calculations).

Composition of electrode in Fig.1(a):

Cathode:  $\text{NaCl} + \text{V}_2\text{O}_5 + \text{AC} + \text{MWCNT} + \text{S} + \text{Cellulose} + \text{Cs}_2\text{NaBiCl}_6$  (0.1 + 0.1 + 0.1 + 0.2 + 0.1 + 0.15 + 0.3)

Anode:  $\text{AC} + \text{MWCNT} + \text{S} + \text{Cellulose}$  (0.08+0.09+0.1+0.13)

It was found that when copper oxide was used in the electrolyte solution, there were redox peaks obtained at different potential ranges and can be seen in Fig.1b and 1c.

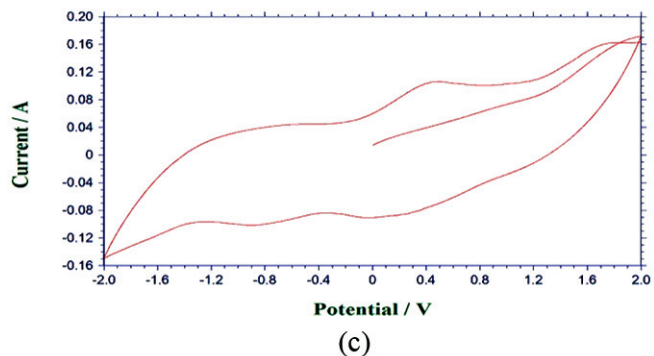
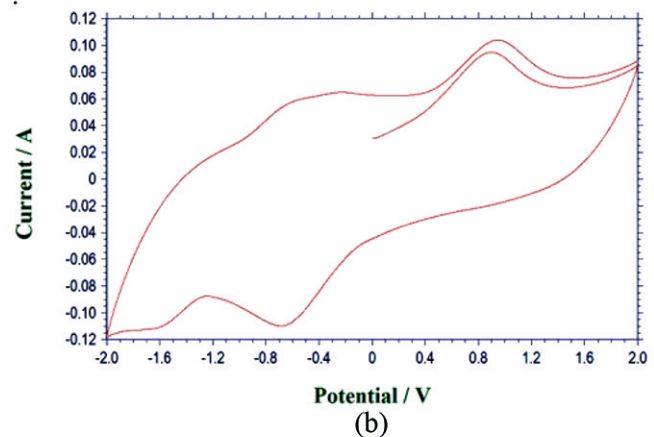
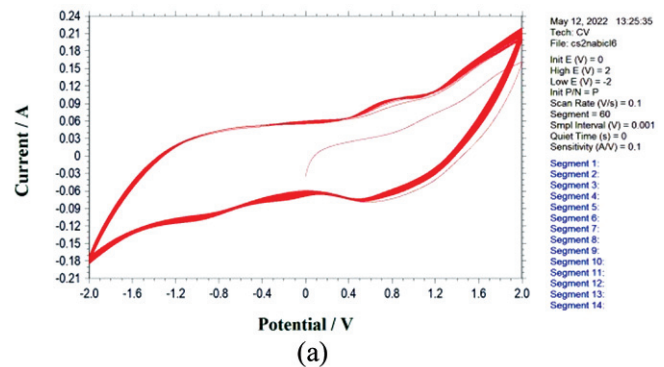


Figure 1(a): CV graph of sodium ion supercapacitor with cathode and anode compositions as above and incorporation of 0.3g  $\text{Cs}_2\text{NaBiCl}_6$ , (b) CV curves between -2V to 2V of base electrode components along with addition  $\text{Cs}_2\text{NaBiCl}_6$  and metal oxide  $\text{V}_2\text{O}_5$  with 1M  $\text{NaClO}_4$  in PC and 0.15 g copper oxide in 5ml ethanol (c) CV curves between -2V to 2V of base electrode components with 1M  $\text{NaClO}_4$  in PC and 0.15 g copper oxide in 5ml ethanol

But when iron oxide was used, there were less prominent redox peaks observed, refer Figs.2(a) and 2(b). The redox peaks in Fig.1(b) and 1(c) correspond to the sodium ion and cuprous ion co-intercalation and de-intercalation from the MWCNT, redox peaks in Fig.2(a) and 2(b) correspond to the sodium ion and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ion co-intercalation and de-intercalation from the MWCNT.

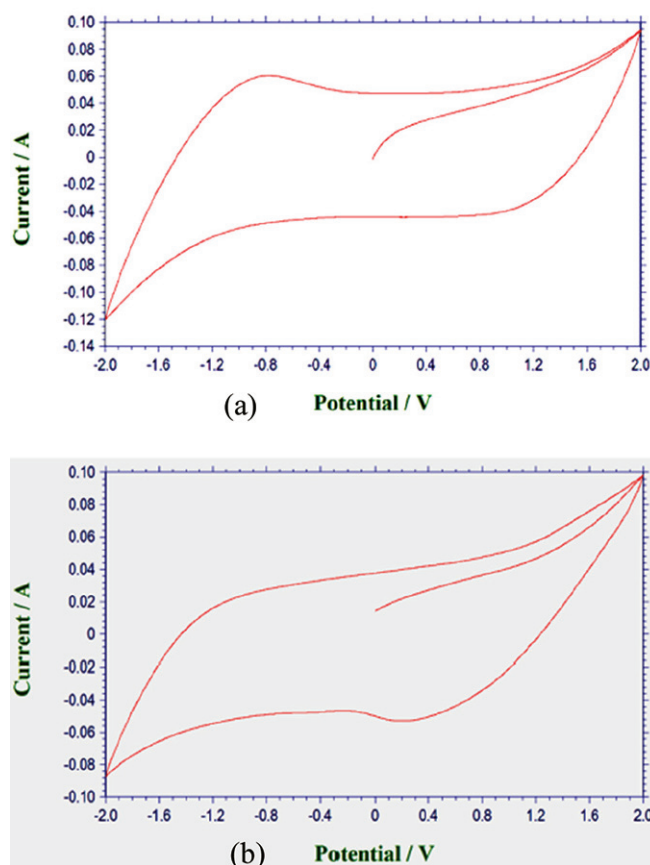


Figure 2(a): CV curves between -2V to 2V of base electrode components with 1M NaClO<sub>4</sub> in PC and 0.15g Iron oxide in 5ml ethanol, (b) CV curves between -2V to 2V of base electrode components along with addition Cs<sub>2</sub>NaBiCl<sub>6</sub> and metal oxide V<sub>2</sub>O<sub>5</sub> with 1M NaClO<sub>4</sub> in PC and 0.15g iron oxide in 5ml ethanol

The current obtained was slightly higher for base electrode components with 1M NaClO<sub>4</sub> in PC and 0.15g copper oxide in 5ml ethanol than the base electrode components along with addition Cs<sub>2</sub>NaBiCl<sub>6</sub> and metal oxide V<sub>2</sub>O<sub>5</sub> with 1M NaClO<sub>4</sub> in PC and 0.15g copper oxide in 5ml ethanol. When base components was used, the

supercapacitor obtained a current value of 0.15 A (Fig.1c) and after addition of metal oxide and Cs<sub>2</sub>NaBiCl<sub>6</sub> the current value obtained is 0.12 A (Fig.1b).

Similarly, the current obtained was slightly higher for base electrode components with 1M NaClO<sub>4</sub> in PC and 0.15g iron oxide in 5ml ethanol than the base electrode components along with addition Cs<sub>2</sub>NaBiCl<sub>6</sub> and metal oxide V<sub>2</sub>O<sub>5</sub> with 1M NaClO<sub>4</sub> in PC and 0.15g copper oxide in 5ml ethanol. When base components were used, the supercapacitor obtained a current value of 0.12 A (Fig.2a) and after addition of metal oxide and Cs<sub>2</sub>NaBiCl<sub>6</sub> the current value obtained is 0.085 A (Fig.2b).

Fig 3a shows the high resolution field emission scanning electron microscope (FESEM) image of the cathode as prepared in Fig.1(a). This shows the porous nanoscale distribution of the perovskite and vanadium oxides in an interlinked fashion. Such a morphology would facilitate easy intercalation and de-intercalation. Fig.3(b) and (c) shows the high resolution FESEM images of the cathode as prepared in Fig.1(c). The electrode shows the interwoven network of the MWCNT which provides easy channels for co-intercalation of Na and Cu ions (from the CuO nanofluid in the electrolyte) and their subsequent de-intercalation.

## 4.0 Conclusion

Novel multifunctional materials were incorporated as cathode coatings as well as electrolyte, for a sodium ion supercapacitor. The multifunctional material used was nanosized perovskite oxide in combination with vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) or modification of electrolyte solution of 1M NaClO<sub>4</sub> in propylene carbonate with nanofluids of copper oxide and iron oxide in ethanol. These nano-oxides are incorporated in addition to cathode nanomaterials like MWCNT, S, cellulose, activated carbon. It is seen that use of the nanosized perovskite oxide and vanadium pentoxide results in higher cathodic current, higher gram capacitance of 33 F/g, energy density of 125 Wh/kg, power density of 20 kW/kg and current carrying capacity of 200 mAh/g. When

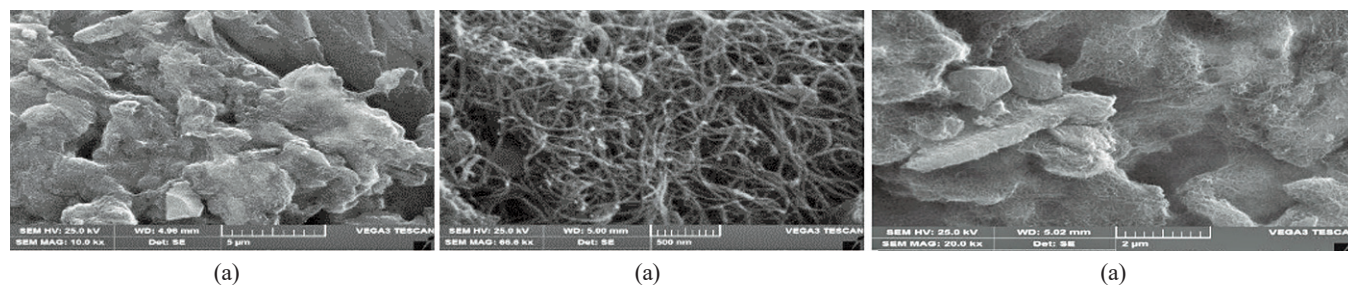


Figure 3(a) Porous nanoscale distribution of perovskite and vanadium oxides are shown (b) FESEM image of cathode corresponding to Fig.1(c). It shows interwoven network of the MWCNTs, which provides easy channels for co-intercalation of Na and Cu ions (from the CuO nanofluid in the electrolyte) and their subsequent de-intercalation. (c) FESEM image of cathode

compared to the CV performance of iron oxide, copper oxide provided better results along with prominent redox peaks. It is observed that the maximum current was obtained when base components was used as electrode materials along with perovskite and vanadium oxides in 1M NaClO<sub>4</sub> electrolyte.

## 5.0 Acknowledgement

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## 6.0 Conflict of Interest

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There are no conflicts to declare.

## 7.0 References

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