



Cite this: *Chem. Commun.*, 2015, 51, 10819

Received 13th April 2015,  
Accepted 26th May 2015

DOI: 10.1039/c5cc03048j

www.rsc.org/chemcomm

## Organoaqueous calcium chloride electrolytes for capacitive charge storage in carbon nanotubes at sub-zero-temperatures†

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**Solutions of calcium chloride in mixed water and formamide are excellent electrolytes for capacitive charge storage in partially oxidised carbon nanotubes at unprecedented sub-zero-temperatures (e.g. 67% capacitance retention at  $-60\text{ }^{\circ}\text{C}$ ).**

Electrochemical capacitors (ECs), also known as supercapacitors, are fast emerging energy storage devices.<sup>1</sup> Current EC research is mainly focused on new electrode materials,<sup>2</sup> but electrolytes are also an essential factor deserving more attention. Electrolytes in ECs can be broadly classified into non-aqueous and aqueous. Non-aqueous electrolytes<sup>3</sup> are based on either organic solvents, such as propylene carbonate, acetonitrile, or ionic liquids (ILs). Organic electrolytes can offer wide potential windows that are needed for high energy storage capacity, but also have high volatility and low flaming points, causing safety concerns. ILs are much less volatile but they are relatively expensive and also too viscous to offer good conductivity. Aqueous electrolytes<sup>4</sup> are usually concentrated solutions of salts, acids or bases. They are restricted by narrow potential windows due to decomposition of water, but have many advantages over non-aqueous electrolytes, such as high conductivity, affordable cost, and low toxicity. These merits of water based electrolytes make them particularly attractive for large scale and stationary applications such as storage of electricity generated from wind turbine farms.

Nevertheless, it is still a challenge to use aqueous electrolytes. Water freezes at  $0\text{ }^{\circ}\text{C}$ , while winds are often stronger and more frequent in places where cold winter often experiences sub-zero temperatures. Hence, for low temperature applications, the

electrolytes used in supercapacitors (and batteries) are commonly non-aqueous,<sup>5</sup> whilst aqueous electrolytes are rarely considered.<sup>6</sup> However, the very recent finding of a specific capacitance value of  $30\text{ F g}^{-1}$  is encouraging by testing the  $\text{MnO}_2$ -carbon composites in mixed water, ethylene glycol and  $(\text{NH}_4)_2\text{SO}_4$  at  $-30\text{ }^{\circ}\text{C}$ .<sup>6a</sup>

It is known that mixing two liquids may lead to eutectic behaviour if hydrogen bonds are involved.<sup>7</sup> In this work, a simple mixture of formamide (FA) and water ( $\text{FA-H}_2\text{O}$ , 1 : 1, v : v) was found to start and finish freezing between  $-32\text{ }^{\circ}\text{C}$  (liquidus temperature) and  $-44\text{ }^{\circ}\text{C}$  (solidus temperature). This liquidus–solidus temperature range (LSTR) is much lower than the melting point (m.p.) of FA ( $2\text{ }^{\circ}\text{C}$ ) or  $\text{H}_2\text{O}$ . This observation can be explained as follows. First, the vapor pressure of any component in a mixture is lower than that of the component alone from the viewpoint of physical evaporation, leading to a LSTR lower than the m.p. of each component. More importantly, FA and  $\text{H}_2\text{O}$  are both hydrogen bond donors and acceptors. As a result, hydrogen bonds are plentiful in the  $\text{FA-H}_2\text{O}$  mixture and can contribute to lowering the LSTR. (Note: we cannot find the  $\text{FA-H}_2\text{O}$  binary phase diagram in the literature and therefore constructed it in this work as presented in Fig. S1 in the ESI.†)

The low LSTR of the  $\text{FA-H}_2\text{O}$  mixture promoted us to use it to dissolve  $\text{CaCl}_2$  for the preparation of low-temperature electrolytes.  $\text{CaCl}_2$  was selected for several reasons. Although not used in past supercapacitor research,  $\text{CaCl}_2$  is a low cost salt with its toxicity (as animal food additive) and water solubility comparable to those of  $\text{NaCl}$ . Also, for road de-icing in winter,  $\text{CaCl}_2$  is widely used mainly because it gives a eutectic temperature of  $-51.6\text{ }^{\circ}\text{C}$ , whilst  $\text{NaCl}$  could only reach  $-21.1\text{ }^{\circ}\text{C}$ .<sup>6c</sup> This ability of  $\text{CaCl}_2$  results possibly from the high affinity between calcium and oxygen. In thermodynamic terms,  $\text{CaO}$  is the most stable metal oxide next to  $\text{CeO}_2$ . This high calcium–oxygen affinity can be translated to that between  $\text{Ca}^{2+}$  ions and the oxygen atoms in water molecules. For the same reason,  $\text{CaCl}_2$  is extremely hygroscopic and often used as a drying agent in laboratory.

We believe that this unique nature of  $\text{CaCl}_2$  can make it a better electrolyte than other common salts, such as  $\text{KCl}$  and  $\text{Na}_2\text{SO}_4$ , for capacitive charge storage on carbon surfaces enriched with e.g. carbonyl, carboxyl and hydroxyl groups or simply oxy-groups.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5cc03048j



In line with this thought, carbon nanotubes (CNTs) were selected for electrochemical tests because CNTs are well-known, particularly after partial oxidation in acids, to possess surface oxy-groups.<sup>8</sup> The affinity of  $\text{Ca}^{2+}$  ions to oxy-groups explains the unique  $\text{Ca}^{2+}$  selectivity of the ionophore A23187 over alkali metal ions (see ESI†). Furthermore, a pure carbon surface is hydrophobic, but because of the oxy-groups, the CNT surfaces are amphiphilic in nature,<sup>8c</sup> and may be better accessed by an organoaqueous electrolyte.

Three  $\text{CaCl}_2$  solutions were prepared using  $\text{H}_2\text{O}$ , FA, or  $\text{FA-H}_2\text{O}$  (vol ratio, 1:1 which was selected to compromise  $\text{CaCl}_2$  solubility, viscosity and liquid temperature range). As expected,  $\text{CaCl}_2$  addition lowered the liquidus temperature to  $-16\text{ }^\circ\text{C}$  for  $\text{CaCl}_2\text{-H}_2\text{O}$  ( $2.0\text{ mol L}^{-1}$ ),  $-41\text{ }^\circ\text{C}$  for  $\text{CaCl}_2\text{-FA}$  ( $1.0\text{ mol L}^{-1}$ ), and below  $-60\text{ }^\circ\text{C}$  for  $\text{CaCl}_2\text{-FA-H}_2\text{O}$  ( $2.0\text{ mol L}^{-1}$ ), respectively.

To prepare the CNT working electrode,  $20\text{ }\mu\text{L}$  aqueous suspension of acid treated CNTs<sup>8</sup> with PTFE (binder, 5 wt% after drying) was dropped on a 5 mm diameter graphite disc electrode, giving rise to a CNT loading of *ca.*  $0.2\text{ mg cm}^{-2}$ . After drying in air ( $>5\text{ h}$ ), the CNT electrode was used to record cyclic voltammograms (CVs) in different electrolytes. A graphite rod and the  $\text{Ag/AgCl}$  couple were used as the counter and reference electrodes, respectively (see ESI† for more details of the three electrode cell).

In this work, temperature control was achieved in two ways. To determine the liquidus and solidus temperatures, an ultralow temperature thermostat bath was used. For cyclic voltammetry, the cell containing 10 mL of the electrolyte was placed in a thermo-container filled with dry ice ( $-78.5\text{ }^\circ\text{C}$ ). A thermocouple was inserted in the electrolyte to monitor the temperature. It was observed that the electrolyte temperature dropped fairly slowly, *e.g.*  $<1\text{ }^\circ\text{C min}^{-1}$  below  $-55\text{ }^\circ\text{C}$ , to enable several CV cycles at a designated temperature and a sufficiently high potential scan rate, *e.g.*  $100\text{ mV s}^{-1}$  (20 s per cycle).

Fig. 1 compares the CVs and specific capacitances of the CNT electrode measured in different electrolytes at  $20\text{ }^\circ\text{C}$  and  $-60\text{ }^\circ\text{C}$ . Fig. 1a shows that at  $20\text{ }^\circ\text{C}$  the CNT electrode behaved almost identically in the  $\text{CaCl}_2\text{-H}_2\text{O}$  and  $\text{CaCl}_2\text{-FA-H}_2\text{O}$  solutions with the CV being highly rectangular in shape, suggesting an insignificant effect of FA on the capacitance of CNTs. In the  $\text{CaCl}_2\text{-FA}$  solution, the CV currents were much smaller, which could be due to the applied  $\text{CaCl}_2$  concentration ( $1\text{ mol L}^{-1}$ ) was already close to saturation and the solution was very viscous. Decreasing the temperature caused a significant impact on the CVs recorded in the  $\text{CaCl}_2\text{-H}_2\text{O}$  and  $\text{CaCl}_2\text{-FA}$  solutions, but much less so in  $\text{CaCl}_2\text{-FA-H}_2\text{O}$  as exemplified in Fig. 1b. Surprisingly, CVs were still recorded in  $\text{CaCl}_2\text{-H}_2\text{O}$  at temperatures below the reported eutectic point,  $-51.6\text{ }^\circ\text{C}$ . These highly reproducible CVs did show noticeably increased resistance in the cell (indicated by the sluggish current switching at both ends of the potential scan), but the currents were not insignificant. This observation indicates the presence of liquid in the cell, likely due to supercooling of the  $\text{CaCl}_2\text{-H}_2\text{O}$  solution (see ESI†).

The capacitance retention ( $C_T/C_{20} = 100 \times$  capacitance at designated temperature/capacitance at  $20\text{ }^\circ\text{C}$ ) of the CNT electrode as derived from the rectangular CVs (see ESI†) is

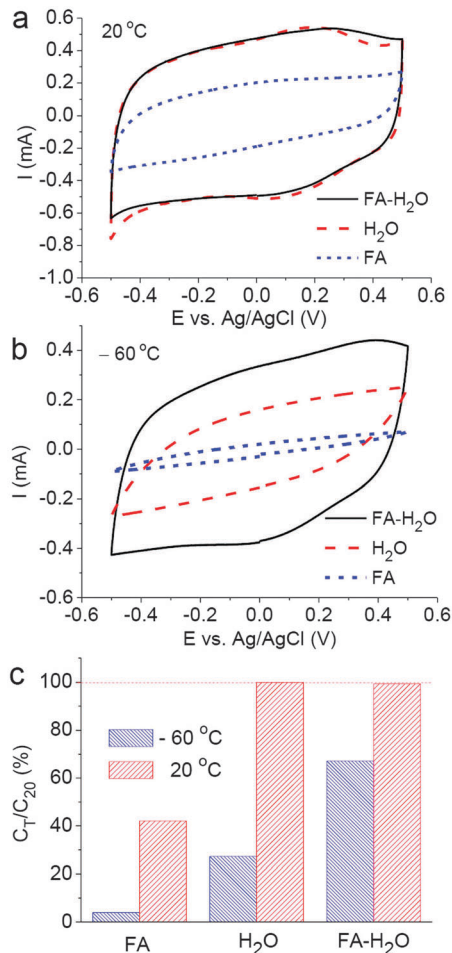


Fig. 1 (a, b) CVs and (c)  $C_T/C_{20}$  of a CNT electrode at (a)  $20\text{ }^\circ\text{C}$  and (b)  $-60\text{ }^\circ\text{C}$  in the  $\text{CaCl}_2$  solution of FA ( $1.0\text{ mol L}^{-1}$ ),  $\text{H}_2\text{O}$  ( $2.0\text{ mol L}^{-1}$ ) and mixed  $\text{FA-H}_2\text{O}$  (1:1, v: v,  $2.0\text{ mol L}^{-1}$ ). Potential scan rate:  $100\text{ mV s}^{-1}$ .

presented in Fig. 1c. At  $20\text{ }^\circ\text{C}$ , the measured specific capacitance,  $C_{sp}$ , was almost the same in  $\text{CaCl}_2\text{-H}_2\text{O}$  ( $108.3\text{ F g}^{-1}$ ) and  $\text{CaCl}_2\text{-FA-H}_2\text{O}$  ( $107.6\text{ F g}^{-1}$ ). In this work, it was observed that the acid treated CNTs exhibited 30–50% higher capacitance in the aqueous solution of  $\text{CaCl}_2$  than that of  $\text{KCl}$  (see Fig. S4 in the ESI†). This difference can be attributed to the greater affinity of the  $\text{Ca}^{2+}$  ions towards the oxy-groups on the CNT surfaces as mentioned above. The fact that each  $\text{Ca}^{2+}$  ion has two positive charges could be another important cause for the increase of the specific capacitance. More discussion is given later and also in the ESI†.

The dependence of specific capacitance on temperature was studied next. In the temperature range from  $20$  to  $-70\text{ }^\circ\text{C}$ , only the  $\text{CaCl}_2\text{-FA-H}_2\text{O}$  solution could remain as a liquid, which is needed to ensure ion mobility and accessibility to the electrode surfaces. Consequently, a meaningful specific capacitance was achieved ( $72.7\text{ F g}^{-1}$  or 67% capacitance retention at  $-60\text{ }^\circ\text{C}$ , see Fig. 1c). Fig. 2a shows the CVs of the CNT electrode in the  $\text{CaCl}_2\text{-FA-H}_2\text{O}$  electrolyte at temperatures varying from  $20$  to  $-70\text{ }^\circ\text{C}$ . In the experiment, the potential was cycled continuously, and the CV was recorded at each of the indicated temperatures in Fig. 2a. It can be seen that the CNT electrode exhibited highly



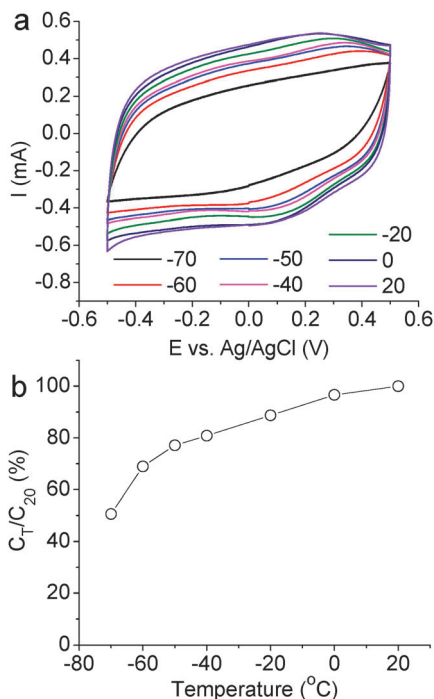


Fig. 2 (a) CVs and (b)  $C_7/C_{20}$  of a CNT electrode in the  $2.0 \text{ mol L}^{-1}$  solution of  $\text{CaCl}_2$  in mixed FA– $\text{H}_2\text{O}$  (1 : 1 v : v) at different temperatures as indicated. Potential scan rate:  $100 \text{ mV s}^{-1}$ .

satisfactory capacitive behaviour (rectangular shape) in the applied temperature range. The CVs decreased in current as temperature decreased, corresponding to the variation of specific capacitance as shown in Fig. 2b. It can be noted that at  $-70 \text{ }^\circ\text{C}$ , the CV is notably separated from that recorded at  $-60 \text{ }^\circ\text{C}$ , which can be explained by the  $\text{CaCl}_2$ –FA– $\text{H}_2\text{O}$  solution under supercooling (see Fig. S1 and S2 in ESI†). Even though, the specific capacitance of the CNT electrode was still measured to be as high as  $53.4 \text{ F g}^{-1}$  or 51% capacitance retention. The cause for the capacitance decay with decreasing temperature may be related to the reduced mobility of ions at lower temperatures. A further contribution to lowering the ion mobility may come from the organo-aqueous solution becoming more viscous upon cooling and supercooling.

Obviously, the dry ice container is not able to offer equilibrium conditions at temperatures higher than that of dry ice. However, as stated above, once placed in the dry ice container, particularly upon the effect of opening and closing the container lid, the electrolyte temperature dropped fairly slowly. At a rate smaller than  $1 \text{ }^\circ\text{C min}^{-1}$ , the difference between CVs continuously recorded at  $100 \text{ mV s}^{-1}$  was very much insignificant. Therefore, the results presented in Fig. 2 can be regarded as recorded under a pseudo-steady state, serving as a practically useful guideline.

The higher specific capacitance of CNTs measured in aqueous  $\text{CaCl}_2$  electrolytes than in KCl warrants more discussion. According to theory, electric double layer capacitance should increase with electrolyte concentration.<sup>9a</sup> This trend agrees with some previous studies of activated carbon in the 1 : 1 type electrolyte such as KCl and KOH in which a double capacitance increase required a 10 fold or greater increase of electrolyte concentration.<sup>9b,c</sup>

To compare a 1 : 1 type electrolyte with a 1 : 2 type, e.g. KCl vs.  $\text{CaCl}_2$ , a simple way was adopted in this work to half the concentration of the latter, e.g.  $1.0 \text{ mol L}^{-1}$  KCl vs.  $0.5 \text{ mol L}^{-1}$   $\text{CaCl}_2$ . The results obtained are presented in Fig. S4 in the ESI† showing clearly higher currents on the CVs recorded in the  $\text{CaCl}_2$  solution at both concentrations. Note that the CNT electrode responded much more significantly to replacing KCl with  $\text{CaCl}_2$  than to doubling the electrolyte concentration. Thus, as discussed above and further in the ESI† (Fig. S6), we believe that the unique interactions between  $\text{Ca}^{2+}$  ions and the CNT surface oxy-groups could have played important roles. This understanding is new to supercapacitor research and, if further proven, could have a significant impact on the development of supercapacitors based on CNTs, graphenes and/or activated carbons which are all enriched with various surface oxy-groups.

In summary, we have demonstrated that mixing  $\text{CaCl}_2$ , FA and  $\text{H}_2\text{O}$  can enable not only very low freezing temperatures, but also excellent capacitive charge storage in CNTs at both room and sub-zero temperatures below  $-60 \text{ }^\circ\text{C}$ . The specific capacitance of the CNTs measured in  $\text{CaCl}_2$  based electrolytes is higher than that in more commonly used alkali salt based electrolytes. This improvement can be largely attributed to the unique affinity between calcium ions and the oxy-groups on the surfaces of carbon nanotubes. We hope that this report can encourage further research on using  $\text{CaCl}_2$  based electrolytes to improve the performance of other carbon materials in supercapacitors.

This work has received financial support from the China Scholarship Council, the EPSRC (EP/J000582/1), and the Ningbo Municipal Government (3315 Plan and the IAMET Special Fund, 2014A35001-1).

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