



Electrochemical studies of acetonitrile based supercapacitor electrolytes containing alkali and alkaline earth metal cations



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ABSTRACT

A series of acetonitrile solutions of the $N(SO_2CF_3)_2^-$ salts of Li, Na, K, Cs, Mg and Ca are examined in a systematic study of electrolytes based on the alkali and alkaline earth series of metal cations. Reference-electrode experiments show that the relatively large and polarisable cesium ion results in the highest capacitance at the negative electrode. We also report current collector corrosion behavior which is anomalously severe for the Mg based electrolyte. Charge-discharge kinetics are investigated using impedance spectroscopy, and it is shown that the new electrolytes have no power advantage over an organic cation based electrolyte at 0.5 M concentration. Constant voltage device testing at 2.7 V and 65 °C reveals a very large electrochemical stability advantage for the K and Cs based devices over the hitherto more commonly studied Li systems.

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1. Introduction:

Supercapacitors provide very high power densities and have the advantage of a generally high cycle life, which makes them the preferred energy storage device for many applications requiring repeated rapid power delivery and/or acceptance. Supercapacitors store energy electrostatically, they use high surface area activated carbon electrodes and electrolytes with high ionic conductivities. During charging electrons are transferred from one electrode to the other via an external circuit, creating a positive and negative electrode. As the supercapacitor is charged, anions from the electrolyte adsorb to balance the charge at the positive electrode, while cations perform the same role at the negative electrode, ion concentration shifts in the bulk electrolyte also occur and are a part of the energy storage mechanism.

Supercapacitors are rated by their capacitance, given in Farads (Coulombs per Volt). A high capacitance capacitor can have transferred a high amount of charge from one electrode to the other for a given voltage increase across the device, and will therefore have a high level of stored energy, given by $E = 1/2CV^2$, where C = capacitance (F) and V = voltage (V).

The capacitance of a supercapacitor is largely determined by the surface area of the carbon, since a higher surface area can accommodate more adsorbed ions, allowing more charge to be accepted onto the electrode for a given potential increase. The closeness of approach, polarisability and charge density of the ions

will all nominally affect their ability to balance the electrode charge, and therefore the electrolyte can also affect capacitance.

Most commercially available supercapacitors use organic electrolytes in order to allow the device to be used at voltages higher than what would be permitted with aqueous electrolytes. These organic electrolytes almost always consist of a quaternary ammonium tetrafluoroborate salt dissolved in either acetonitrile or propylene carbonate.

A moderate amount of research into alternative supercapacitor electrolytes has been done in recent years, covering such families of chemicals as ionic liquids [1], sulfones [2] and dinitriles [3]. Unfortunately, a lack of long duration constant voltage, elevated temperature testing in many studies means that the real stability of these systems is not always properly assessed. This has unfortunately led to many premature claims of high operating voltages being achieved. Testing device electrochemical stability by cycling is a deeply flawed concept, since the activated carbon electrode does not go through any kind of phase change, and since only at the top of the cycle (near V_{max}) do the electrodes reach extreme enough potentials to cause degradation reactions to occur—therefore most of the cycle does not stress the cell, and even an unstable cell can take more than a year of cycling to show its weakness. A test at 65 °C, rated voltage, for 1000 h (with cell characteristics measured at RT every ~200 h) or until the cell loses 20% of capacitance is an industry standard test which evaluates electrochemical stability much better than room temperature cycle testing.

Systematic studies of different organic cations in non-aqueous solvents have shown how capacitance and resistance, which

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dictate energy and power respectively, can be affected by changes in cation size and shape [4–6]. However, electrolytes based on metal cations in organic solvents have been infrequently studied and there are few publications that allow fair comparisons to be made between different metal cations. As such, the fundamental capacitance behavior of the different cations dissolved in organic solvents relative to each other is not well understood. Although a picture has emerged, albeit a rather patchy one, of generally disappointing stability for these systems (mostly Li based), to the best of our knowledge, there has never been a systematic evaluation of device stability across a broad range of metal cations in an organic solvent. Since there are some obvious, if conceptual, possible advantages of using metal cations instead of organic cations, it is desirable to increase the fundamental and practical understanding of this class of electrolytes.

To help put this study into context it is worthwhile to explore some of the advantages that metal cations conceivably have over organic cations. Quaternary ammonium and quaternary phosphonium cations are the most reductively stable organic cations available, they typically undergo gross reduction at or beyond -2.8 V (vs. SHE) [7], and in some situations the stability may be extended to nearly -3 V (vs. SHE) such as when the materials are of exceptional purity or when large alkyl groups are used. Although phosphonium cations have been studied as potential electrolyte salts [4,8,9], and have even been proven to be of equal stability to quaternary ammonium cations in some cases [4], to the best of our knowledge phosphonium cations are not being used in commercial supercapacitors, instead quaternary ammonium cations are preferred. The reduction potentials of alkali metal cations in organic solvents are expected to be similar or even better than that of a quaternary ammonium cation, however metal cation reduction potentials for any system will depend on both the solvent type [10] and the anion.

Quaternary ammonium cations undergo ion-dipole interactions with the highly polar acetonitrile in solution, and in addition the quaternary ammonium cation itself can exist in a number of conformations within the electrolyte. Variations in coordination and conformation may impact the reductive (and thermal) stability of the cation to some extent, therefore low levels of electrochemical reduction (i.e. the reduction of cations in unstable conformations) may occur prior to the gross reduction onset potential. Metal ions will also be coordinated to acetonitrile, but since they are monoatomic they are, of course, not subject to conformational instability. Any background level reduction of a metal cation preceding the gross reduction onset potential should be less than in the case of organic cations. In supercapacitor applications this may be a very important issue, since it is only the background level redox reactions that lead to device failure, rather than a breach of the gross electrochemical limit.

Low level thermal degradation of quaternary ammonium cations may initiate at about $70\text{ }^\circ\text{C}$ in the presence of activated carbon [11] (although bulk thermolysis requires higher temperatures). Obviously there is no possibility of the thermal degradation of a metal ion, thus a possible weak link in the electrolyte chain is removed by switching to a metal cation.

Any reduction of the alkali or alkaline earth metal cation that does occur will produce the reactive metal itself, the metallic surface may well react with acetonitrile or trace impurities in the electrolyte. The overall effect would most likely be the passivation of the electrode. In the case of a non-spiro quaternary ammonium cation, reduction by the Hoffman elimination route will liberate gaseous products (increasing pressure in the cell), unsaturated hydrocarbons as well as a tertiary amine [7]. The amine will likely cross the separator and undergo oxidation at the positive electrode at about 1 V (vs. SHE) [12], or react with any H^+ generated at the positive electrode. The unsaturated species may

undergo addition reactions, potentially forming precipitating products and contributing to electrode passivation. Overall, the presence of the organic cation opens the door to a wide range of reactions, and yields a potent cocktail of degradation products that may otherwise be avoided simply by switching to a metal cation. However, to repeat, as yet there have been no stability advantages observed for metal cation systems.

The small size of the metal cations may allow more of the activated carbon's pore space to be utilized, beneficially affecting the overall capacitance. The high charge density and closeness of approach to the carbon surface may also have a positive effect on capacitance due to the fact that the capacitance will increase as the charged planes (carbon surface and adsorbed ion layer, in this case) become closer together. By virtue of their Lewis acid character, metal ions may also influence the dielectric properties of any acetonitrile molecule that is adsorbed on the carbon surface. Of course the high charge density may have an adverse effect as well by way of a possibly lower polarisability compared to an organic cation, adversely affecting the dielectric behavior. In Table 1 we give the polarisabilities and radii of the alkali and alkaline earth cations. As one would expect, there are large increases in polarisability as the radius of the cation increases through both the alkali and alkaline earth series.

Whether there is any economic or environmental advantage of using a metal cation over a hydrocarbon type cation would have to be assessed on a case by case basis. For example lithium and cesium both have commercial applications, but they are quite rare and relatively expensive elements, and would not be the preferred solution from a price and sustainability viewpoint. Possible disadvantages of using metal cations include: lower electrolyte conductivity, higher self discharge, destructive intercalation behavior with carbon electrodes and the ability of the metal cation to form passivating metal salts (such as metal hydroxides) during the course of electrolyte side reactions. The known reduction product of acetonitrile $(\text{CH}_2\text{CN})^-$ [17], should it occur

Table 1
Characteristics of alkali and alkaline earth ions

Ion	Effective ionic radius, C.N. [‡] =4 (Å) †	Effective ionic radius, C.N.=6 (Å) †	Volume (Å ³)	Charge density (e/Å ³)	Polarisability (a.u.) ^{d,†}
Li ⁺	0.59*	0.76	1.13	0.881 (C. N.=4)	0.19
Na ⁺	0.99*	1.02	5.36	0.186 (C. N.=4)	0.99
K ⁺	1.37*	1.38	14.20	0.070 (C. N.=4)	5.35
Rb ⁺		1.52*	19.39	0.0512 (C. N.=6)	9.07
Cs ⁺		1.67*	25.72	0.038 (C. N.=6)	15.81
Fr ⁺		1.8*	32.21	0.031 (C. N.=6)	20.4
Be ²⁺	0.27	0.45*	0.50	3.974 (C. N.=6)	0.052
Mg ²⁺	0.57	0.72*	2.06	0.970 (C. N.=6)	0.47
Ca ²⁺		1*	5.52	0.362 (C. N.=6)	3.25
Sr ²⁺		1.18*	9.07	0.220 (C. N.=6)	5.81
Ba ²⁺		1.36*	13.89	0.143 (C. N.=6)	10.61
Ra ²⁺		1.48 ^{ab}	17.90	0.112 (C. N.=8)	13.36
TEA	3.42 ^a		159 ^c	0.0063	

[‡]C.N.= coordination number. †Dean [13], ‡Mitroy et al. [14], ^aUe et al. [15], ^bC. N.=8 for Ra²⁺, ^cVan der Waals volume [16], ^d1 a.u.=0.14818 Å³=1.64877 × 10⁻⁴¹ C. m²/V, *used to calculate volume since this is the likely C.N. in acetonitrile.

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