Design considerations for ionic liquid based electrochemical double layer capacitors

Vitor L. Martins [a, b, *], Roberto M. Torresi [b], Anthony J.R. Rennie [a, **]

[a] Chemical and Biological Engineering, University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield S1 3JD, England, UK
[b] Depto. Química Fundamental, Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes 748, 05508-000 São Paulo, SP, Brazil

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ABSTRACT

A critical parameter in the design of EDLCs is the determination of electrochemical stability limits for individual combinations of electrode and electrolyte. Using [EMIm][BF$_4$] as an example we demonstrate that the physical properties of the activated carbon used in the electrodes influence the permissible operating potential of an EDLC, and also that the binder material employed can have further effects. When [EMIm][BF$_4$] electrolyte is coupled with electrodes containing PTFE binder, operating potentials as wide as 3.8 V can be utilised. Due to the differences in response under opposing polarisations, it is necessary to employ an asymmetric mass loading in EDLC cells in order to make full use of the operating window. By balancing the charge in the cell, the differences in stable potential limits and capacitative behaviour can be overcome, however we also found that this balance can be influenced by the rate at which these parameters are determined. Three-electrode measurements show that using an appropriate mass loading ratio results in each electrode operating within their determined stability limits. Stable cycling of a full cell at an operating potential of 3.8 V was demonstrated over 50,000 cycles.

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1. Introduction

Electrochemical energy storage devices are key facilitators for the widespread adoption of renewable energy sources and electrochemical double layer capacitors (EDLCs) are a class of such devices that store energy at the interface between an electrode and electrolyte [1—4]. The electrochemical stability of this interface defines the safe operating potential of such devices and, in turn, determines its energy and power handling characteristics. Electrolytes that are usually found in EDLCs comprise a solution of a conducting salt in an organic solvent and have been demonstrated to withstand operating potentials as high as 3.5 V [5]. Ionic liquids (ILs) have attracted a lot of attention relating to their use as electrolytes due to their large electrochemical stability windows [6—8]. As they do not require any solvent to render them ionically conductive, and typically show a high level of thermal stability, ILs can also be considered as a safer electrolyte for EDLCs [9—11].

Among the most widely studied ILs used as EDLC electrolytes are 1-ethyl-3-methyl tetrafluoroborate ([EMIm][BF$_4$]) [6,12—22] and N-butyl-N-methyl- pyrrolidinium bis(trifluoromethane sulfonyl imide) ([Pyr$_{1,4}$][Tf$_2$N]) [6,8,23—26]. In the latter case, operating potentials up to 3.9 V have been demonstrated [26], however performance is hindered by the relatively high viscosity and low ionic conductivity of the IL (78 mPa s and 3.0 mS cm^{-1} at 25 °C [27]). [EMIm][BF$_4$] typically operates over a smaller potential window (up to 3.5 V) but performs better at higher rates due to its more favourable physical properties (37 mPa s [16] and 14 mS cm^{-1} at 25 °C [28]). Furthermore, it has been shown that mixtures of ILs can demonstrate improved characteristics when compared to the pure IL. For instance low temperature operation is made possible using IL mixtures [20,29,30]. Alternatively, Van Aken et al. [31] reported that mixtures of ILs can also extended the maximum operating voltage of EDLCs, prolonging the cycle life of symmetrical devices.

A crucial parameter when assessing suitability of an IL as an EDLC electrolyte is the determination of a stable operating voltage, however there is no definitive method by which to determine this and as a result, a range of operating potentials have been reported for individual ILs [32]. Typically, stability limits have been identified using a specific current density [6,15,33] or value of coulombic efficiency [27,34—39], both methods that rely on the selection of

* Corresponding author. Chemical and Biological Engineering, University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield S1 3JD, England, UK.
** Corresponding author.
E-mail addresses: martinsv@iq.usp.br (V.L. Martins), a.rennie@sheffield.ac.uk (A.J.R. Rennie).

arbitrary cut-off values calibrated toward each individual system. However a more reliable technique for the determination of stable operating potentials has been developed by Weingarth et al. [17]. A modified version of this method is used in this work to investigate the effects that different carbon materials and binders can have on the electrochemical stability of [EMIm][BF$_4$].

In this work it is shown that the electrochemical stability of [EMIm][BF$_4$] in EDLCs is not independent of the electrodes used as the type of activated carbon as well as the nature of the polymeric binder play a major role in the determination of a suitable operating potential. We also show that operating at different rates can result in individual electrodes operating beyond their stability limit.

2. Experimental

[EMIm][BF$_4$] (>99%, 'for electrochemistry') was purchased from Fluka and was dried by heating at >100 °C with vigorous stirring for several hours in an argon-filled glovebox (H$_2$O < 0.1 ppm, O$_2$ < 0.1 ppm). Karl-Fischer titration (KF899, Metrohm) was used to determine the moisture content of the ILs before use and was found to be less than 10 ppm after the drying procedure.

EDLC electrodes were prepared by mixing an activated carbon, conductive carbon black (Super C45, Imerys) and PVdF or PVdF-HFP in 80:10:10 ratio by mass using 1-methyl-2-pyrrolidone (anhydrous 99.5%, Sigma-Aldrich). Each slurry was then spread using an adjustable gap paint applicator to a wet film thickness of 150 μm on 15 μm thick aluminum foil. Sheets were dried at 80 °C under vacuum prior overnight prior to being punched into individual electrodes with 12 mm diameter. A similar procedure was used to produce electrodes using sodium carboxymethylcellulose (CMC, Sigma-Aldrich) as binder, using deionized water rather than 1-methyl-2-pyrrolidone.

In order to obtain counter electrodes with at least 10 times the active mass compared with conventional electrodes, the same composition described previously was used with PTFE (Teflon 30-N, Alfa Aesar) as binder in ethanol. This produced self-supporting electrodes with a thickness of approximately 600 μm. (PTFE bound working electrodes were produced by calendering the above mixture to a thickness of roughly 50 μm).

Cell were assembled using two electrode button cells (2016) with stainless steel spacers, electrodes, and glass fibre filter paper as separator (GF/F, Whatman). The separator was impregnated with the IL and the cell was placed under vacuum in the glovebox antechamber for at least 5 min to encourage thorough wetting of the electrodes. Cells were sealed inside the glovebox. Swagelok™ type three-electrode cells were assembled using the same materials as for coin cells with 0.5 mm diameter silver wire as a pseudo-reference electrode.

Electrochemical stability windows were investigated using a modified version of the technique proposed by Weingarth et al. [17], using electrodes with a mass at least 10 times greater than the working electrode, as described elsewhere [27,39,40]. Four cyclic voltammograms were performed in these asymmetric cells from the open circuit potential (OCP) to 0.5 V (*vs* OCP) at 5 mV s^{-1}. After that, the window was increased in increments of 0.1 V to a maximum of +2.0 V (*vs* OCP). The same procedure was performed using fresh cells from OCP to −1.0 V (*vs* OCP), to a maximum of −3.0 V (*vs* OCP). Δq-values were calculated from the last cycle at each electrochemical window, and stability limits identified by a sharp rise in the value of d^2(Δq)/dV^2. Cyclic voltammetry was performed using a Solartron Analytical 1470E Multi-channel Potentiostat/Galvanostat.

The electrochemical performance of EDLCs were evaluated by cyclic voltammetry using scan rates from 5 to 500 mV s^{-1}. The specific capacitance, C_{CV}, was determined from the charge delivered during the discharge process, $\int i \cdot dt$, the operating potential window, U, and the active mass of both electrodes (total mass of activated carbon in cell), m, as shown in Equation (1):

$$C_{CV} = \frac{\int i \cdot dt}{U \cdot m} \tag{1}$$

Cells were cycled galvanostatically between 0 V and the determined operating voltage at different rates from 0.1 to 10 A g^{-1}, using a Maccor 4000 M cell test system. Specific capacitance, C_{GC}, was determined considering the current, i, the slope of the discharge curve after iR drop, dV/dt, and the active mass, m, as shown in Equation (2):

$$C_{GC} = \frac{i}{(dV/dt) \cdot m} \tag{2}$$

Specific energy, E_{ave} and specific power, P_{ave}, were determined from the galvanostatic experiments considering the current, i, operating voltage, U, time of discharge, t_d, and both electrodes active mass, m, using Equations (3) and (4):

$$E_{ave} = i \cdot \int \frac{U}{m \cdot 3.6} \cdot dt_d \tag{3}$$

$$P_{ave} = \frac{E_{ave} \cdot 3600}{t_d} \tag{4}$$

Cycle life was investigated by cycling cells between 0 and the stated operating potential at 2.0 A g^{-1} using a Maccor 4000 M cell test system. Cells were maintained at 25 °C using an environmental chamber unless stated otherwise.

3. Results & discussion

Five different carbon materials were used to produce electrodes using PVdF binder. Three of the materials (A, B and C) are commercially available carbons used widely in EDLC electrodes. Carbons D and E are described as conductive carbon blacks with high specific surface area. Electrodes containing carbons A, B and C were fabricated using 10% wt. of carbon black and 10% wt. PVdF binder, however carbons D and E required a greater mass fraction of PVdF to produce mechanically stable electrodes and no carbon black was needed. Results from carbons D and E were obtained from electrodes comprising 80% wt. carbon and 20% wt. PVdF. The carbons possess important different physical and textural properties that are considered in the following discussions; they are described and illustrated in Supplementary Material, in Table S1, Figs. S1—S3.

3.1. Electrochemical stability of [EMIm][BF$_4$] with different carbon materials

Fig. 1 shows the results of stability determinations for [EMIm][BF$_4$] conducted in a manner similar to that described by Weingarth et al. [17]. In this method, cells with a highly asymmetrical mass loading are cycled potentiodynamically to increasing vertex potentials, with the quantity of charge passed in each step being recorded. These measurements are then expressed in terms of a stability factor, or 'S- value' which is equivalent to 1- (Q$_{discharge}$/Q$_{charge}$). However, during the course of this work it was necessary to adjust the criteria to allow for the use of different activated carbon materials and alternative binders, as well as different electrolytes. For this reason, the results are presented in a slightly