



Influence of aqueous electrolyte concentration on parasitic reactions in high-voltage electrochemical capacitors



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ABSTRACT

Increasing operating voltage is a straightforward approach to increase the specific energy of aqueous electrolyte based electrical double-layer capacitors (EDLCs). A broader operating voltage window, however, comes at the expense of accelerated cell ageing processes. Two complementary *in situ* gas analysis techniques, i.e., internal cell pressure measurement and Online Electrochemical Mass Spectrometry (OEMS), were applied to study the influence of electrolyte salt concentration on the electrochemical degradation of the electrode and decomposition of electrolyte during cycling of symmetrical carbon based EDLCs. Higher concentrations of Li_2SO_4 aqueous electrolyte salt increase the coulombic efficiency of the cell and reduce the amount of volatile side reaction products (e.g., CO , CO_2 , and H_2) arising from carbon corrosion and water electrolysis. The lower amount of degradation products when increasing the salt to solvent ratio is believed to result from a favorable stabilization of the increasingly coordinated electrolyte solvent-salt bonds, which in turn increases the energy barrier for H_2O decomposition. Higher salt concentrations not only increase the electrochemical reversibility at high cell voltages but also increase cell charging capacities as a result of increased electrolyte conductivity, which all-in-all facilitates implementation of future high energy aqueous EDLCs.

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1. Introduction

Electrochemical capacitors are electrochemical energy storage devices for rapid power storage and delivery [1–3]. Immense research efforts have for decades focused on improving critical performance parameters of EDLCs, such as the specific energy/power, cycling stability, safety, and cost [4]. Insufficient specific energy is currently one of the major bottlenecks for introducing EDLCs in further commercial applications [5]. A typical activated carbon based EDLC has a gravimetric energy density of ~ 10 Wh/kg [6]. In order to increase the EDLC specific energy, one may enhance the specific capacitance (C) by development of the specific electrode surface and/or introducing pseudocapacitive redox species. On the other hand, increase the cell voltage (U) appears to be the reasonable approach since the energy stored in EDLCs is described by the relation: $E = 1/2CU^2$ [7].

Aqueous electrolyte-based EDLCs operating in acidic or alkaline solutions exhibit high power rates and large capacitance values, although at moderate cell voltages ($U < 1.2$ V). Such an operating voltage is a significant limiting factor compared to EDLCs based on

non-aqueous electrolytes [8]. Notwithstanding, the symmetrical activated carbon-based EDLCs containing 1 M Li_2SO_4 aqueous electrolyte were recently demonstrated to operate stably at voltages up to 2.2 V with a specific capacitance of 120 F/g at reasonable discharging currents ~ 0.2 A/g [9]. Despite the promising energy/current densities, cell ageing issues were found to be more pronounced at high operational voltages ($U > 1.6$ V), which consequentially compromised the long-term cycling and safety performance of the device [10].

Ageing phenomena in high-voltage aqueous EDLCs include electrolyte depletion, carbon corrosion [11], activated carbon surface area loss [10], current collector corrosion [12], increased cell impedance [13], and internal cell pressure build-up [14]. The performance loss is often related to a complex interplay between these various ageing processes, and a definite judgement of the cause of cell failure is often difficult, particularly when the cell chemistry is analyzed *ex situ* (or *post mortem*) after cycling. Therefore, research efforts are increasingly focusing on *in situ* or *in operando* analytical techniques to monitor the processes governing the cell performance during cycling. We have recently demonstrated that *in situ* gas analysis may provide valuable insights into electrode/electrolyte degradation reactions of high-voltage aqueous EDLCs [11]. The extent, type, and potential onset of various electrolyte/electrode side-reactions can be studied in detail by

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registering the evolution of volatile species in the cell by *in situ* cell pressure and online electrochemical mass spectrometry (OEMS) measurements. The aim of the current study is to demonstrate the influence of electrolyte salt concentration on parasitic side reactions in high-voltage symmetrical activated carbon EDLCs based on aqueous lithium sulfate electrolytes. Since the electrolyte salt concentration is well known to influence the physicochemical properties of the electrolyte (e.g., density, conductivity, and viscosity [15]) and has previously been shown to affect the electrochemical performance of high-voltage aqueous EDLCs significantly [9,16], we investigate its influence on electrolyte decomposition and carbon corrosion.

2. Experimental

2.1. Materials and electrochemical cell assembly

Self-standing carbon electrodes were punched out from an activated carbon tissue (ACC 507-20, Kynol, Germany) with a diameter of 14 mm for the pressure cell ($m_c = 18 \pm 0.3$ mg) and 18 mm for the OEMS cell ($m_c = 30 \pm 0.3$ mg), respectively. Physical and chemical properties of the activated carbon material have been characterized and introduced elsewhere [11]. Three different concentrations of Li_2SO_4 electrolytes, namely 0.1, 1.0, and 2.5 M, were prepared by dissolving analytical quality Li_2SO_4 salt (> 99.99%, Sigma-Aldrich, Switzerland) in deionized water.

Electrochemical cells, including pressure and OEMS cells as described elsewhere [11], were assembled in a symmetrical cell configuration containing two identical carbon electrodes, a glass fiber separator, and a fixed amount of Li_2SO_4 electrolyte (200 μL for pressure cell, 250 μL for OEMS cell). Three hours of equilibrium time was applied to all assembled cells prior to electrochemical cycling in order to obtain a stable pressure background.

2.2. *In situ* gas characterization

Working principles of both *in situ* pressure cell and OEMS technique have been introduced in our previous studies [11,17,18]. For a cell pressure measurement, the internal pressure change was recorded uninterruptedly by a pressure transducer upon cycling [17]. In OEMS measurement, evolved gases were continuously carried out from the head space of OEMS cell by a controlled Ar flow to the inlet of the mass spectrometer (MS) [11]. The partial pressure of gas species in Ar flow was documented as MS ion-current intensity. In order to quantify the amount of evolved H_2 and CO_2 , mass signals of $m/z=2$ and 44 were calibrated with standard calibration gases (0.5% H_2 in Ar 5.0 gas, 0.1% CO_2 in Ar 5.0 gas, Messer, Switzerland). The time-lag of gas detection was estimated about 30 s corresponding to a considerable potential shift of 0.3 V at 10 mV/s cyclic voltammetry sweep rate. Thus, a slower sweep rate of 1 mV/s was employed for OEMS measurements.

2.3. Electrochemical cycling

Cyclic voltammetry (CV) was performed by a computer controlled potentiostat/galvanostat (CCCV hardware, Astrol Electronic, Switzerland) with cell voltage windows of 0–1.0, 0–1.2, 0–1.4, 0–1.6, 0–1.8, and 0–2.0 V at a sweep rate of 1 mV/s. The extent of coulombic charge and capacitance loss of the EDLCs was studied by galvanostatic cycling at a current density of 0.2 A/g and voltage range of 0–2 V.

3. Results and discussion

Fig. 1a shows the CV profiles with a step-wise increasing voltage window for every cycle of symmetrical EDLC cells containing 0.1, 1.0, and 2.5 M concentrations of Li_2SO_4 aqueous electrolyte. The lower ionic conductivity of the 0.1 and 1.0 M electrolytes is observed as a resistive character of the corresponding CV profiles compared to the more rectangular shaped CV profile for the 2.5 M electrolyte. The EDLC with the highest salt concentration displays the highest specific capacitance (~ 130 F/g), which is in line with the result of Sun et al. [16], who reported that the charge-transfer resistance of EDLC cells decreased while the capacitance and rate capability increased with higher electrolyte salt concentrations. However, the difference in capacitances is minor as higher salt concentrations also increase electrolyte viscosity and bring the active ions on carbon surface closer to their saturation [9]. The resistive character of the CV profile is also further pronounced after the cell was polarized at $U > 1.6$ V (arrow, Fig. 1a), particularly for the electrolytes with low salt concentrations, which possibly reflects an increased electrolyte resistance due to side-reactions at high cell polarizations. Galvanostatic cycling ($j_m = \pm 0.2$ A/g, 2 V cut-off voltage) in Fig. 1b similarly shows that both the specific capacitance as well as the reversibility are improved at high electrolyte salt concentration. The EDLC cell with 2.5 M electrolyte provides a specific discharge capacity Q of 36 mAh/g, and the fading of Q may be attributed to the precipitation of salt or its decomposition products, which in turn could block the active pores of the carbon electrode during long-term cycling [10,13]. A more recognizable capacity fading, from initial Q of ~ 35 mAh/g to a steady Q of 28 mAh/g, is observed in the EDLC cell with 1 M electrolyte, which could be related to a combined effect of electrolyte solvent and salt decomposition during the initial conditioning cycles. The EDLC cell with 0.1 M electrolyte salt concentration displays the lowest specific capacity and reversibility, which is in line with previous observations [9,16], and is believed to be related to the lower electrolyte conductivity and pronounced electrolyte solvent decomposition. In conclusion, EDLC cells with higher electrolyte salt concentrations display better electrochemical performance in terms of capacity and coulombic efficiency, which are believed to be related to lower extents of irreversible electrolyte side-reactions.

Fig. 2a shows the cell voltage (U), specific current (j_m), and internal cell pressure (P) profiles of symmetrical EDLC cells filled with 0.1, 1.0, and 2.5 M Li_2SO_4 electrolyte, respectively, during three consecutive CV cycles in voltage ranges from 1.0 V, 1.2 V, 1.4 V, 1.6 V, 1.8 V to 2.0 V. Both the faradic currents and irreversible cell pressure increases are, similarly to observations in Fig. 1, markedly pronounced at higher cell voltages. Lower electrolyte salt concentrations result in higher cell pressure ($\Delta P \sim 20$ mbar for 0.1 M Li_2SO_4 and 9 mbar for 2.5 M Li_2SO_4), which thus reflects a pronounced influence of parasitic side reactions and the volatile side products. Regardless of electrolyte salt concentration, partly reversible cell pressure fluctuations ($\Delta P \sim 1$ to 2 mbar) are, as previously observed [11], superimposed on irreversible cell pressure increase and are most likely related to reversible gas evolution/consumption processes. The gas evolution rate (r_{gas}) inside the closed electrochemical cell can be roughly estimated according to the ideal gas law (an increase of 1 mbar/min g pressure would approximately correspond to a r_{gas} of 77 nmol/min g at room temperature). Two separated r_{gas} peaks (indexed as peak 1 and 2 in Fig. 2a, for 1 M Li_2SO_4) are discernable throughout the cycling, and are believed to be related to oxidation of carbon surface groups (e.g., $(\text{RCO})_2\text{O} \rightarrow \text{CO}_2/\text{CO}$, $U < 1.4$ V) and direct carbon corrosion ($U > 1.6$ V) processes, respectively [11]. Side reactions related to the current collector were prevalent during cycling but accounted for by identically cycled cells (blank in Fig. 2a, for 1 M

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