Voltage limitation of supercapacitors by charge-induced strain and gas evolution.

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Abstract—**Experimental support is provided that the voltage limitation of today's supercapacitors (SC) using aprotic electrolytes is governed by two processes, pressure build-up by solvent electrolysis and electrode swelling due to ion insertion. The insertion of the large quarternary ammonium cations resulting in a pronounced electrode swelling is found to be the major process limiting the cathodic potential range to ≥ 1.5 V vs. Li/Li$^+$. On the other hand, the anodic stability range is primarily limited by solvent oxidation to ≤ 4.5 V vs. Li/Li$^+$. In order to quantify the amount of gases formed upon electrolysis we measured the pressure increase during (over-) charging of a SC device. Electrochemical dilatometry was used to determine the charge induced electrode expansion. The behaviour of the commercial activated carbon based SC electrode is compared with that of a graphite electrode.**

I. INTRODUCTION

Charge storage in today's supercapacitors (SC) is ideally assumed to take place in the high surface area carbonaceous electrodes at the large inner boundary between the porous solid and the aprotic, organic electrolyte solution by means of electrostatic charge separation [1]. According to this picture, no structural changes occur during charging/discharging, and the upper voltage limit is solely determined by the stability of the solvent against electrolysis. In the present contribution we show that this concept is likely to be too simplistic. By means of electrochemical dilatometry evidence is provided that ion insertion takes place well within the usual operation range of 2.5 V. In fact, the insertion of the large R_4N^+ cations is found to be the process limiting the cathodic potential range, while the anodic stability range is mainly controlled by solvent oxidation. In order to quantify the amount of gases formed upon electrolysis we measured the pressure increase during (over-) charging of a SC device using the propylene carbonate based standard electrolyte.

II. EXPERIMENTAL

A. Electrochemical Dilatometry

The electrochemical measurements were carried out with a home-made dilatometer [2]. Basically, the set-up consists of two electrodes separated by a stiff glass frit fixed in position. An aluminium foil is positioned on top of the upper working electrode (WE) and serves as the current collector as well as the electrolyte sealing. Also, this foil transmits any height change of the WE via a moveable plunger to a displacement transducer. Free-standing electrodes (5 to 10 mm in diameter) as well as binder-free powders can be used as the WE material. After assembly in air, the dilatometer cell (with the displacement transducer detached) was dried for 24 h at 120 °C and 0.01 mbar, then cooled down to ambient temperature in argon atmosphere, transferred to a glove box (argon, <10 ppm water) and finally filled there with the electrolyte solution, 1 M $(C_2H_5)_4NBF_4$ (TEABF$_4$) in propylene carbonate (battery grade, <20 ppm water). Measurements were performed in a test cabinet at constant temperature (25 °C ± 0.1 °C). An electrochemical workstation (IM6, Zahner electric, Germany) was used for electrochemical instrumentation. All potentials were measured against an activated carbon (M150) pseudo reference, but were later converted against Li/Li$^+$ for clarity (carbon vs. Li/Li$^+$ = 3.0 V ± 0.05 V).

B. Pressure Measurement

The set-up used to measure the pressure build-up inside a capacitor cell upon charging has been described in detail in [3]. Basically, a D-size electrode coil (350 F rated capacitance, containing about 25 cm^3 of activated carbon M150) is mounted inside a stiff housing. The electrode coil consists of two aluminum foil supported activated carbon electrodes with a paper separator in between. Prior to measurement, the cell is vacuum dried (24 h, <1 mbar, 130 °C), then cooled down in argon atmosphere and transferred to a glove box (argon, <10 ppm O$_2$ and H$_2$O). Inside the glove box, the cell is connected to a pressure transducer (0 to 6 bar abs.) and a dispenser. The assembly is filled with about 40 ml of the argon saturated electrolyte solution, then discharged from the glove box and finally placed into a temperature chamber held at 25 °C ± 0.1 °C.

During the experiment the compressibility of the set-up is determined by periodic injection/removal of a small electrolyte volume ΔV. The corresponding pressure change ΔP is recorded as an extra hump on the otherwise smooth pressure curve. From the ratio $(\Delta V / \Delta p)_p$ the gas volume

change is calculated according to $V_p = \int_{p_0}^{p} (\Delta V / \Delta p)_p \, dp$.

The measurement is performed in the two-electrode arrangement without a reference electrode.

C. Carbon Materials

Height change and gas pressure build-up were measured on a proprietary activated carbon based SC electrode (M150, Maxwell Technologies SA, Switzerland). Dilatometric measurements were also performed on non-porous graphite with spherical particle shape (MCMB25-28, Osaka Gas, Japan).

III. RESULTS AND DISCUSSION

A. Dilatometry
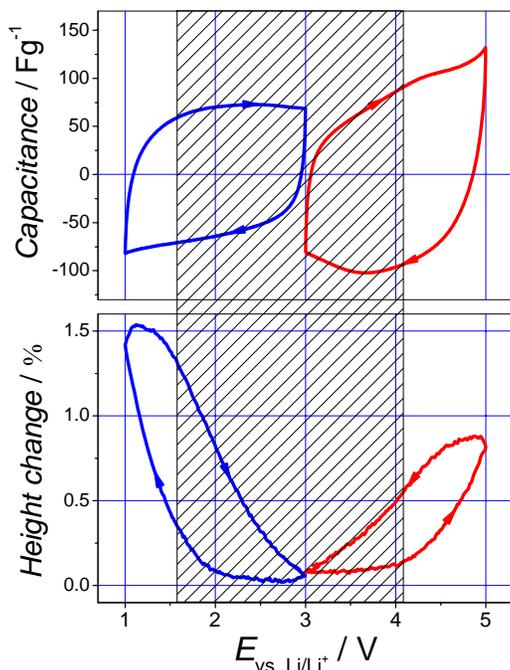
Fig. 1. Current response (top) and simultaneous height change (bottom) of the activated carbon electrode (M150) during CV experiment. Only the 4th cycle is shown. Scan rate: 5 mV/s. Applied load: 2 N. The shaded area roughly indicates the standard SC operation range of 2.5 V. The current is normalised to the weight of the dry carbon and to the sweep rate, thus yielding the gravimetric differential capacitance.

Fig. 1 shows the cyclic voltammograms (CV) and the simultaneous height change of the activated carbon electrode, M150. The electrode was first cycled between the rest (zero charge) potential, about 3.0 V vs. Li/Li$^+$, and a lower (cathodic) limit of 1.0 V vs. Li/Li$^+$. Subsequently, the same electrode was cycled in the anodic range, 3.0 V to 5.0 V. For both polarities, only the 4th cycle is shown. The coulombic efficiency, defined as the ratio of the charge released during the backward scan and the charge accommodated during the forward scan, approaches ca. 97 % (4th cycle) for the cathodic range and only 90 % (4th cycle) for the anodic range. At the same time, the electrode shows considerable expansion, up to

2 % for the cathodic range, and significantly less, about 1 % for the anodic range. Quite obviously, the observed periodic height change can be attributed to ion insertion and extraction. The higher charge specific expansion for the negative potential range can be attributed to the larger ion diameter of TEA$^+$ (0.69 nm) as compared to BF$_4^-$ (0.46 nm), or to the different solvation of the inserted ions. However, the precise nature of the insertion sites is presently not fully understood. To address this question, X-ray and Raman microscopic investigations are underway.
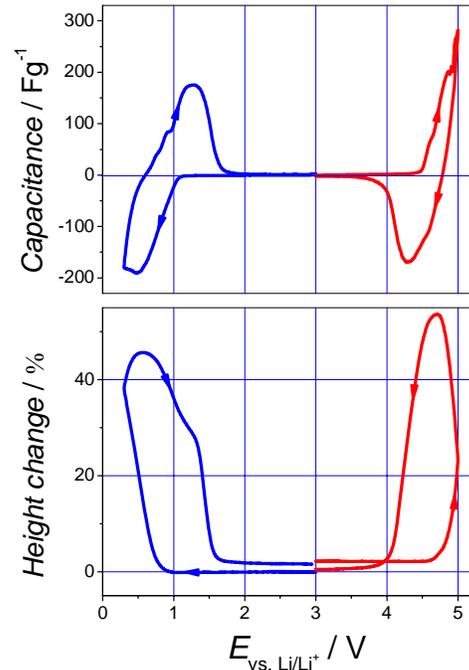
Fig. 2. Current response (top) and simultaneous height change (bottom) of a powder type graphite electrode (MCMB). Scan rate: 1 mV/s. Electrolyte: 1 M TEABF$_4$ in propylene carbonate. Applied load: 2 N.

In clear contrast to M150, distinct current peaks are observed for the intercalation of both TEA$^+$ and BF$_4^-$ into MCMB (Fig. 2). For this highly graphitic material, the onset of intercalation and simultaneous expansion is clearly defined. Cation insertion commences at 1.0 V, anion insertion at 4.3 V vs. Li/Li$^+$ and thus more remote from the potential of zero charge than for the activated carbon. The charge specific expansion of MCMB, however, is almost two orders of magnitude larger than that of M150.

B. Gas Evolution

Fig. 3 shows the evolved gas volume V computed from the pressure curve recorded during subsequent hold periods at stepwise increased cell voltages of 2.5, 2.75, and 3.0 V [3]. For each voltage step, the volume curve is reset to t = 0 and V = 0. The pronounced gas evolution during first charging (t < 2 h, 2.5 V) is in agreement with previous differential electrochemical mass spectrometry (DEMS) measurements [4] and might indicate some electrochemically induced wetting of the electrodes. Assuming ideal gas behaviour, gas evolution rates dn/dt of 0.5, 1.4, and 3.3 µmol/hour can be derived at

t = 15 h for 2.5 V, 2.75 V and 3.0 V, respectively. Further on, relating the gas evolution to the residue current i by means of Faraday's law yields z, the number of electrons corresponding to the formation of one gas molecule: $z = i / (F \, dn/dt)$, where F is the Faraday constant. The results shown in Fig. 4 clearly reveal that at all cell voltages only a minor part of the leakage current results in gas formation. During the initial hold period at 2.5 V z drops to about 450 electrons per gas molecule. The corresponding values at 2.75 and 3.0 V are 140 and 65, respectively.
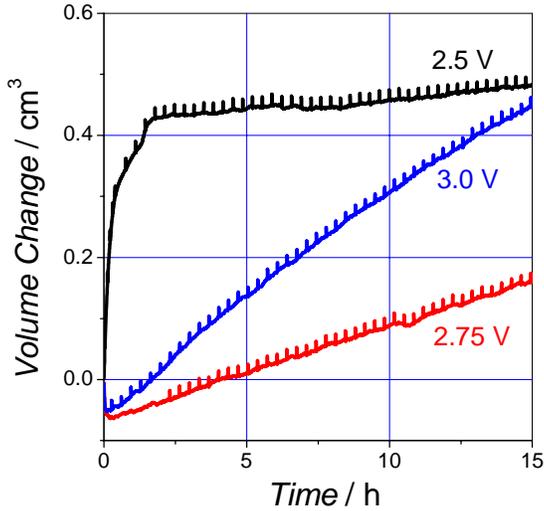
Fig. 3. Evolved gas volume (calculated for p = 1 bar) during subsequent hold periods at stepwise increased cell voltages (single experiment). Data adopted from [3].

In contrast to the earlier DEMS investigation [4], the present pressure measurement does not allow for on-line determination of the evolved gases. However, it is possible to take samples with a syringe and analyse the gas composition off-line. First results of a GC/MS analysis indicate propene and CO_2 as main products, confirming our earlier results [4].
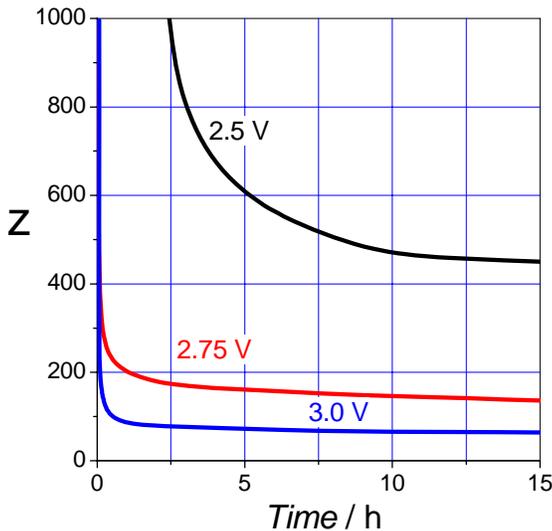
Fig. 4. Number of electrons corresponding to the formation of one gas molecule. Data adopted from [3].

IV. CONCLUSIONS

The dilatometric results suggest that insertion processes play an important role for the voltage limitation of today's supercapacitor technology. The expansion of SC type activated carbon electrodes is, within the rated voltage range of 2.5 V, only about 1% and hence smaller than that of the graphite electrode in the lithium-ion battery (ca. 3%). However, with increasing SC voltage, expansion rises steeply and therefore will soon reach the acceptable limits. As the tolerable expansion will strongly depend on the mechanical design of the housing, a flexible (foil pouch) case could be a pre-requisite for higher SC voltages. Further work is required to understand the possible impact of periodic dimensional changes on life time issues.

Already for a cell voltage of 2.5 V, gas evolution becomes detectable during voltage hold experiments at room temperature. The absolute amount of gas evolved could be calculated on the basis of compressibility measurements during the experiment. The results indicate that most of the leakage current results into other processes than gas evolution.

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