Pressure Evolution and Analysis of Aged Electrodes at High Temperature in Electrochemical Double Layer Capacitors

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The internal pressure of electrochemical double layer capacitors (EDLCs) using 1.0 mol dm⁻³ triethylmethylammonium tetrafluoroborate (TEMABF₄) in acetonitrile at different voltages at 70°C was measured and sources of the internal pressure were clarified. The PCLV (precharge at low voltage) method was used to weaken the gas evolution and decrease internal pressure. It was found that the EDLC dealt with the PCLV had lower pressure at high voltage than that which was not. Electrochemical impedance spectroscopy was used to measure the capacitance and resistance of the EDLC after ageing. Elemental composition and morphology of the electrodes were analyzed by FESEM-EDX. The gas products generated at 3.0 V were identified by GC-MS. The reaction mechanisms of gas evolution are discussed.

Key Words: EDLC, Ageing, Gas Evolution, Internal Pressure

1 Introduction

Electrochemical double layer capacitors (EDLCs), also called supercapacitors and ultracapacitors, have made rapid development recently because they show irre- placeable power densities (1-10 kW kg⁻¹), which is much higher than that of lithium-ion batteries (0.1-1 kW kg⁻¹). In addition, their life time (10⁶ cycles) is much longer than batteries (10⁵ cycles), so they are widely used in the energy storage systems, wind power systems and hybrid vehicles. But their energy densities (10 Wh kg⁻¹) are lower than lithium-ion batteries (100-200 Wh kg⁻¹), which is also the main reason why EDLCs cannot replace lithium-ion batteries completely.

EDLCs can be divided into two categories according to electrolytic solutions. One kind is utilizing aqueous electrolytes containing mineral acids, but its working voltage is limited to 1.23 V because of water decomposition in the electrolytes, so it has the shortness of low energy densities. The other kind is composed of nonaqueous electrolytic solutions with alkylammonium salt dissolved in one or more organic solvents such as propylene carbonate (PC), acetonitrile (AN), sulfolane derivatives and so on. The operational voltage of this EDLC can be increased to 3.35 V, which improves energy and power densities. Then the significant question appears which is prevalent in the lithium-ion batteries. Namely, thermal effect will come into being, so gases, which come from thermal evaporation, especially from chemical reactions and electrochemical reactions on the surface of the electrodes, greatly increase the internal pressure in such narrow space during charge and discharge process. This not only damages performance of the EDLC, but also poses a safety threat when the EDLC ruptures resulting from high pressure. There are many papers about the gas evolution of lithium-ion batteries. Lanz’s study showed that gas evolution in lithium-ion batteries developed during the first 10 min of electrochemical charging. Holzapfel found that oxygen evolution happened on the oxidative reaction of the LiCoO₂ electrode and the addition of vinylene carbonate decreased the CO₂ evolution in lithium-ion batteries. Shin detected gaseous products including CO₂, CO, CH₃, C₂H₄ and C₃H₆ in 1.0 mol dm⁻³ LiPF₆ in ethyl carbonate/dimethyl carbonate and ethyl carbonate/diethyl carbonate electrolytes. Goers et al. discovered that PC-containing electrolytes caused large amounts of gas, while electrolytes based on γ-butyrolactone (GBL) showed the evolution of only very small amounts of gas. However, only a few literatures concerning such gas evolution regarding supercapacitors are reported up to now. For example, Kötzt et al. monitored gas evolution and associated pressure in commercial EDLCs using 1.0 mol dm⁻³ solutions of TEABF₄ in AN, PC. During the voltage hold (24h) experiments, they found severe gas evolution in PC started only at 3.0 V, while in AN rate of gas evolution remained low even at 3.25 V. Hahn’s research indicated that C₂H₄ and CO₂ were main decomposition products for the cell voltage above 2.5 V. Ishimoto et al. detected CO₂ and CO in the positive electrode, CO₂, CO and C₂H₆ in the negative electrode using chromatography method. They applied the SEI theory to illustrate the change of the surface of AC electrode after the float test performed on the EDLC.

In this paper, the internal pressure evolution of com-
mercial EDLCs using 1.0 mol dm$^{-3}$ TEMABF$_4$ in AN was investigated at various ageing voltages at 70°C. The method of precharge at low voltage (PCLV) was tried to decrease the internal pressure. The causes and reaction mechanisms of gas evolution were discussed.

2 Experimental

2.1 Internal pressure observation

EDLCs (KAM 350F) from Jinhzhou Kaimei Power Co. Ltd. (China) are employed. The capacitor consists of 1.0 mol dm$^{-3}$ solution of TEMABF$_4$ in AN. The parameters about the applied electrolyte are given in Table 1.

The EDLC sample was attached to the pressure transducer in the glove box filled with high purity argon. The experiment condition was defined as an ambient temperature of 70°C (Fig. 1). The volume of the device was 5.65 mL. The pressure increased from 0.100 MPa ($P_1$) to 0.151 MPa ($P_2$) after the sample was placed in the drying oven. To investigate the internal pressure at different voltages with time, first two groups of experiments were designed as follows:

(1) Sample-1, sample-2 and sample-3 were first charged to 2.5 V, 2.7 V, and 3.0 V at a current of 2 A, respectively, and then constant voltage was applied for 40 hours.

(2) To cancel out the errors brought by different samples used at various constant voltages, the same sample (Sample-4) was applied as trapezoidal voltage as shown in Fig. 2. The sample was held at 2.3 V, 2.5 V, and 2.7 V for 10 hours respectively, 3.0 V for 5 hours and 3.3 V for 0.6 hours.

2.2 Electrochemical impedance measurements

The same EDLC sample was applied different voltages (2.5 V, 2.7 V, 3.0 V, for 40 hours). After each constant voltage process, the sample was discharged to open circuit voltage (0.1 V). Then the capacitance and resistance were measured by electrochemical impedance spectroscopy with a frequency range at 10 kHz to 10 mHz. The measurements were conducted using a VMP2 (Princeton Applied Research) with EC-Lab software (version 9.30).

2.3 Elemental composition and morphology of positive and negative electrodes

The positive and negative electrodes of the fresh sample and the above sample aged at 3.0 V for 40 hours at 70°C were rinsed in AN for 12 hours and dried at 120°C in vacuum for 24 hours. Elemental composition and morphology change were observed by FESEM-EDX (Zeiss Supra TM 55 microscope).

2.4 Gas analysis

The above sample aged at 3.0 V for 40 hours at 70°C was cooled to room temperature, and then gaseous products were collected. Gas chromatography mass spectrometry (GC-MS) (Thermo Finnigan, Trace DSQ) was served to ascertain elements and the proportions of the gas products. The injection volume was 10.00 μl.

3 Results and Discussion

3.1 Calculation of initial pressure in EDLCs

The pressure value increased from 0.1 MPa ($P_1$) at 298.15 K($T_1$) to 0.151 MPa($P_2$) at 343.15 K($T_2$) when the EDLC sample was put into the oven (343.15 K). According to equation of ideal gas ($PV=nRT$), the pressure value at 70°C should be 0.115 MPa. We explain the contradiction as follows.

The pressure increase can be attributed to two reasons. At first, the internal space of the device was full of argon. When the device was put in the oven, the growth of pressure caused by argon can be calculated by the following formulas:

![Fig. 1 Sketch map of the equipment of measuring the internal pressure of the EDLC.](image)

![Fig. 2 Trapezoidal voltage applied to sample-4.](image)
\[
\frac{P_{\text{AN}25}}{T_1} = \frac{P_{\text{AN}70}}{T_2} = \frac{P_{\text{AN}70} - P_{\text{AN}25}}{dP_{\text{AN}}} = \frac{dP_{\text{AN}}}{dT} \tag{1}
\]

\[
\frac{0.101 \text{ MPa}}{298.15 \text{ K}} = \frac{dP_{\text{AN}}}{dT} \quad 45 \text{ K}
\]
\[
dP_{\text{AN}} = 0.015 \text{ MPa}
\]

On the other hand, the electrolyte solutions contain AN which has high vapor pressure and high volatility, but the saturated vapor pressure of the solutions will be lower than pure AN on the basis of colligative properties of solutions. The first step is to get the saturated vapor pressure of AN at 70°C. Two values of saturated vapor pressure of pure AN at two different temperatures are acquired according to reference. At temperature \(T_1\) (293.15 K), the value \(P_1\) is 9700 Pa. At temperature \(T_2\) (300.15 K), the value \(P_2\) is 13330 Pa. So we can calculate the saturated vapor pressure value \(P_s\) at 343.15K \((T_s \approx 70 \text{ °C})\) according to Clausius-Clapeyron equation as follows:

\[
\ln \frac{P_s}{P_1} = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_s} \right)
\]

\[
\ln \frac{P_s}{P_2} = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_s} \right)
\]

Then, the value of saturated vapor pressure \(P_s\) of the pure AN at 343.15 K is 0.071 MPa. So we calculate the growth of pressure \(dP_{\text{solvent}}\) caused by dilute solution based on Raoult’s law:

\[
dP_{\text{solvent}} = P_s x_{\text{solvent}}
\]

In the above equation, \(x_{\text{solvent}}\) is the mole fraction of solvent in dilute solution. Here, the molar concentration of the electrolyte is 1.0 mol dm\(^{-3}\) and density is 0.94 g cm\(^{-3}\), so \(x_{\text{solvent}}\) is calculated as follows:

\[
x_{\text{solvent}} = \frac{\text{Solute}}{\text{Solvent}} = \frac{\frac{1000\text{g} - \text{Mol} \text{Solute}}{\text{Mol} \text{Solvent}}}{1 + \frac{1000\text{g} - \text{Mol} \text{Solute}}{\text{Mol} \text{Solvent}}}
\]

\[
= \frac{940 - 203.03}{1 + 41.05} = 94.7\%
\]

In the equation, \(M_{\text{solvent}}\) and \(M_{\text{solute}}\) represent molecular weights of the solvent and solute, respectively. \(dP_{\text{solvent}}\) is calculated out by the following.

\[
dP_{\text{solvent}} = P_s x_{\text{solvent}} = 0.071 \times 0.947 = 0.067 \text{ MPa}
\]

The theoretical value of the internal pressure of the device at 343.15 K (70°C) is calculated as follows

\[
P = P_0 + dP_{\text{AN}} + dP_{\text{solvent}} = 0.100 \text{ MPa} + 0.015 \text{ MPa} + 0.067 \text{ MPa} = 0.182 \text{ MPa}
\]

It can be seen that the theoretical value is greater than the actual value (0.151 MPa), this is because part of the device was out of the oven.

3.2 Internal pressure changes in EDLCs at constant voltages process

The correlation between internal pressure of the three samples and time can be seen clearly from Fig. 3 (a). The pressure increases dramatically in the first 3 hours. Then it shows slow growth from the 3\(^{rd}\) hour to the 30\(^{th}\) hour, meaning that electrochemical decomposition reactions which give off gas become stable, and tends to be smooth from the 30\(^{th}\) hour. The pressure curves of sample-1 and sample-2 are close to each other, while the pressure of sample-3 is much larger, indicating that severe gas evolution happens at 3.0 V.

During the voltage hold experiments the leakage current of the EDLC was monitored continuously and is plotted in Fig. 3 (b). The leakage currents of sample-1 and sample-2 were below 10 mA from the 10\(^{th}\) hour. On the contrary, it is not easy for the leakage current of sample-3 to drop down below 10 mA because of side reaction at 3.0 V. Same to the pressure change, the leakage current curves of sample-1 and sample-2 are essentially coincident with each other, implying that the mechanisms of gas evolution at 2.5 V and at 2.7 V are identical.

Additionally, the pressure growth rates of the three samples can be acquired by the differentiation of pressure curves as the function of time. As can be seen from Fig. 3 (c), three plots show the biggest values at the time of 0.25 h, this is because at the beginning large current results in severe decomposition of electrolyte. The pressure growth rates appearing gentle in later period and having little difference are due to decrease of leakage current. Also it is easier for the electrolytes (AN, HBF\(_4\), for example) to decompose electrochemically at 3.0 V than that at 2.7 V and 2.5 V, so the maximum rate at 3.0 V is larger than that at 2.5 V and 2.7 V.

**Fig. 3** (a) The internal pressure, (b) the leakage current, and (c) the pressure growth rate of samples 1, 2, 3 at various constant voltages for 40 hours at 70°C as a function of time.
The internal pressure change of sample-4 is displayed in Fig. 4 during trapezoidal voltage. It can be seen that the pressure still shows slow and linear growth though the voltage increases from 2.3 V to 2.5 V and from 2.5 V to 2.7 V, indicating that the mechanisms of gas evolutions at 2.3 V, 2.5 V and 2.7 V are identical, which is in accordance with Fig. 4. The difference of the pressure growth at 3.0 V and at 3.3 V illuminates different gas evolution mechanisms.

To further study the relationship between voltage and pressure, the method of precharge at low voltage (PCLV) was tried. For example, sample-5 was firstly held at low voltage (2.5 V) for 10 hours, then was charged to 2.7 V and was held for 40 hours. As a comparison, sample-6, which was not dealt with PCLV (2.5 V), was also charged to 2.7 V and held for 40 hours. Fig. 5 (a) shows the interesting difference of these two samples. It can be clearly seen that the internal pressure of sample-5 is lower than that of sample-6. The same results can be seen in Fig. 5 (b). The results demonstrate that EDLC dealt with PCLV tends to have less gas evolution. Thus, it is feasible to use this method to weaken the gas evolution of EDLC effectively. It is considered that the composition resulting in gas evolution may be transferred to other forms at low voltage. Further study is under work.

3.3 Impedance change after ageing

Figure 6 shows the Nyquist plots of a fresh EDLC and that after ageing process at different voltages for 40 hours. It is obvious that all of the plots conform to the typical characteristics of an EDLC, and are composed of the slope changing from 45° to 90° in the lower frequency range.21 But the intersection of these plots with the real axis (Im Z = 0) shifts to high value as the voltage increases. At such high frequency, the EDLC behaves like a pure resistor. Therefore, the abscissa of the intersection correlates well with the equivalent series resistance (ESR) measured by discharging with direct current.22 So it is deduced that the ESR has the increasing trend with the increasing voltage.

According to Taberna’s work, EDLC can be regarded as a whole, and then it is possible to define

\[ C(\omega) = C'(\omega) - jC''(\omega) \] (7)

\[ C'(\omega) \text{ and } C''(\omega) \text{ can be calculated based on the following formulas:} \]

\[ C'(\omega) = \frac{-Z'(\omega)}{\omega |Z(\omega)|^2} \] (8)

\[ C''(\omega) = \frac{Z''(\omega)}{\omega |Z(\omega)|^2} \]

Where the \( Z'(\omega) \) and \( Z''(\omega) \) are the real part and the imaginary part of the impedance data, respectively. The value of \( C'(\omega) \) at low frequency shows the capacitance change of the EDLC that is measured in constant current discharge mode. \( C'(\omega) \) is the imaginary part of the capacitance \( C(\omega) \). It corresponds to energy dissipation by an irreversible process.20

The change of real capacitance \( C'(\omega) \) reflects the characteristics of pore structure of the activated carbon electrode structure and the electrode/electrolyte interface. EDLC behaves like a resistor at high frequency, so the capacitance approaches zero because of not making full use of the pore, as shown in Fig. 7 (a). Moreover, it can be seen that the value of \( C'(\omega) \) shifts to low value with the increasing voltage at low frequency. This is because more decomposition products at high voltage block the
pore of activated carbon electrode which results in attenuation of capacitance.

Figure 7 (b) shows the $C'$ ($\omega$) plots as a function of frequency. All the plots display maximum value at a certain frequency, and this frequency is called characteristic frequency ($f_0$), with the time constant defined as $\tau_0 = 1/2\pi f$. In the RC circuit, when power supply charges the capacitor through the resistance, the voltage on the capacitor is slowly established and the charging current changes from maximum to zero. The speed of this process is measured by the time constant $\tau_0$. The larger $\tau_0$ is, the longer transition process of the circuit is, that is to say, the circuit needs more time to achieve steady state. This process can be described by the following formula:

$$U_c = U[1 - \exp(-\frac{t}{\tau})]$$

(9)

Where $U_c$ and $U$ are the voltages of the capacitor and the power supply, respectively, $t$ and $\tau$ are the charging time and time constant. From Fig. 7 (b), it is revealed that the characteristic frequency (66.5 mHz) of the fresh EDLC remains unchanged after ageing at 2.5 V and 2.7 V for 40 hours at 70 °C, while the characteristic frequency drops to 55.4 mHz after it was aged at 3.0 V on the same conditions. In addition, the value of $C'$ ($\omega$) becomes smaller and smaller at low frequency with the increasing ageing voltage, which indicates that energy dissipation gets more and more serious.

3.4 Changes of elemental composition and morpholo- gy

Based on the above analysis, the performance (including decrease of capacitance and increase of time constant) of EDLC began to decline from 3.0 V. In view of the above facts, the electrodes were investigated by FE-SEM-EDX.

As can be seen from Fig. 8 (a), the fresh electrode shows rough surface which can supply more capacitance, but the positive electrode (Fig. 8 (b)) and negative electrode (Fig. 8 (c)) of the EDLC after ageing at 3.0 V show smooth surfaces failing to offer high capacitance. In other words, some films of substances are visible on the surface of the positive electrode and negative electrode. The films of substances increase ionic conduction resistance and lower the capacitance, which is in accordance with the analysis of impedance. It may be explained by the following EDX analysis.

EDX spectra of the three electrodes are shown in Fig. 9. All exhibit C and O peaks which are ascribed to activated carbon and oxygen functional groups on the surface of activated carbon. Most of N is originated from side reactions of AN. Noticeably, two new elements (Al and F) appear on the positive and negative electrodes. Moreover, the content of F on the positive electrode is about seven times as much as that on the negative electrode. The content of Al is also respectable on the positive electrode.

A film of compact oxide ($\text{Al}_2\text{O}_3$) covers the aluminum foil which served as the current collector, it will react with traces of acid existing in the electrolyte ($\text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- = 2\text{Al}^{3+} + 3\text{H}_2\text{O}$). There are HF due to hydrolysis of HBF$_4$ so AlF$_3$ will be generated ($\text{Al}^{3+} + 3\text{HF} = \text{AlF}_3 \downarrow + 3\text{H}^+$). AlF$_3$ is insoluble in most organic solvents, so it will deposit on the surface of the activated carbon, as shown in Fig. 8. It may result in resistance increase and capacitance decrease.

3.5 Analysis of gas products and reaction mecha- nisms

Based on above analysis, severe gas evolution happened to the EDLC aged at 3.0 V for 40 hours at 70 °C. The final pressure was 0.332 MPa and the initial pressure was 0.151 MPa. The pressure increased by new decomposition products was 0.181 MPa, translates to molar quantities of new products as $0.356 \times 10^{-3}$ mol (calculated by $n = PV/RT$). GC-MS was applied to analyze the gas composition. Figure 10 is the attained chromatogram of the gas that was produced at 3.0 V (70 °C). We can see five obvious peaks at retention times of 1.66 min, 1.72 min, 1.84 min, 4.81 min and 12.31 min which represent
CO₂, C₂H₆, C₂H₄, CH₂CF₃, and C₂H₇F, respectively.

The relative content of the gases calculated by the area of each integration peak is shown in Table 2.

It can be seen from Table 1 that there are existing traces of water in the electrolyte, so the hydrolysis reactions of AN and HBF₄ will happen (CH₃CN + H₂O = CH₃CONH₂, CH₂CONH₂ + H₂O = CH₂COONH₂, HBF₄ + H₂O = H [BOF₄] + 2HF). The acetate is oxidized to CH₃CHO and CO₂ (2CH₃COO⁻ = CH₃CHO + CO₂ + 2e⁻). Besides, quaternary ammonium salt will decompose when heated ((C₅H₅N)₂CH₂N⁻ → (C₅H₅CH₂N) + C₂H₅⁺). On the other hand, the free radical will react with BF₄⁻ (C₂H₅⁺ + BF₄⁻ = C₂H₅ + HBF₄⁻). On the other hand, it combines with F⁻ from ionization of HF (C₂H₅⁺ + F⁻ = C₂H₇F). There is an unsaturated bond in AN molecule, so addition reaction will happen (CH₃CN + 4HF = CH₂CF₃+[NH₄]⁺+F⁻).

4 Conclusion

The initial internal pressure of the EDLC is lower than the theoretical value on the basis of colligative properties of solutions. The internal pressures of the EDLCs aged at 25 V and at 27 V at 70°C have the same evolution trends during the 40 hours basically. Severe gas evolution happens to the EDLC aged at 3.0 V for 40 hours at 70°C. The pressure at various voltages became stable from about the 30th hour. The pressure growth rates show the largest values at time about 0.25 h.

To weaken the gas evolution, the method of precharge at low voltage (PCLV) was put forward. The experimental results indicate that the EDLC which is dealt with PCLV had lower pressure at high voltage than that one which was not.

Through the impedance spectroscopy, it could be deduced that the performance of the EDLC aged at 3.0 V for 40 hours at 70°C is lowered. This may results from some films of substances depositing on the surface of activated carbon which can be observed by FESEM. The films of substances can increase ionic resistance and lower capacitance because of smooth surface. It is found that the film of substances are composed by C, N, O, Al and F through EDX analysis.

The decomposition products which were generated at voltage of 3.0 V were identified by GC-MS. Gas products included CO₂, C₂H₆, C₂H₄, CH₂CF₃, and C₂H₇F. The mechanism involving hydrolysis reactions and free radical reactions was discussed.

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