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Nondisruptive In Situ Raman Analysis for Gas Evolution in Commercial Supercapacitor Cells

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ABSTRACT

This paper proposes novel nondisruptive in situ Raman spectroscopy analysis for gas evolution in commercial supercapacitor cells. To accelerate gas evolution, abusive aging tests were conducted during 21 days using commercial supercapacitor cells with a Raman setup. Changes in partial pressure were recorded using the Raman setup after the aging tests under various electrochemical analysis, such as cyclic voltammetry (CV), galvanostatic charge/discharge analysis, and impedance spectroscopy. The performance of the bare supercapacitor cell was evaluated and compared with that of the Raman cell. Difference of capacitance derived from CV was less than 1% until end of life of the cells. Moreover, resistance results obtained from galvanostatic charge/discharge differed below 8%. This analysis confirmed that the Raman cell was nondisruptive with a minute effect on the supercapacitor cell itself, indicating high reliability of in situ gas analysis of practical cells.

1. Introduction

Supercapacitors have gained widespread attention among the research community as promising energy storage devices because of their superior power density and longer life cycle compared to secondary batteries. For example, the electric double layer capacitors (EDLCs) are supercapacitors that store charge electrostatically within the electric double layer at the electrolyte/electrode interphase. Recently, EDLCs have gathered increasing attention in research because they can be applied to new emerging applications, such as for load leveling in renewable energy systems and as devices for digital communications, electric vehicles (EVs), and hybrid electric vehicles (HEVs) [1–6]. Despite their high specific power property, EDLCs have intrinsic low specific energy than secondary batteries because of their low capacitance per electrode area on the order of several microfarads per square centimeter and low operating potential [7,8]. To increase the energy density, a high operating voltage is desirable because both power and energy density are proportional to V^2 [1,2]. In the case of an operating voltage increase, the life time of EDLCs has been reported to reduce drastically; their relationship can be described using a power law [9]. In particular, the degradation at an elevated cell potential is primarily attributed to decomposition of solvent (e.g., acetonitrile and propylene carbonate), which causes gas accumulation within the cell. The accumulated gas increases inner pressure, which weakens device stability and reduces the cycle life [9–12]. Temperature, being another important factor affecting EDLC performance, was considered to determine the cycle life of EDLCs. Recently, R. Kotz et al. reported that voltage elevation is a more dominant factor than temperature elevation [13]. Hence, both voltage elevation and temperature increase can accelerate gas evolution in supercapacitors.

To clarify the gas evolution mechanism, electrolyte decomposition with gas evolution has been extensively investigated. Most scientists employed the gas chromatograph–mass spectrometer (GC-MS) technique. For example, the evolution of gases and water from activated carbon electrodes was observed during a floating test at 4.0 V and 60 °C for 50 h. Carbon oxides such as CO and CO_2 were detected in the positive compartment. Hydrocarbons such as propylene, ethylene, and carbon oxides were evolved in the negative electrodes [14,15]. However, analysis based on GC-MS has several disadvantages such as disassembly of the cell during the charge and discharge processes and collection of evolved gas samples by using a microsyringe. These disadvantages mean that cell chemistry can be disrupted during the sampling process, which should be repeated for detailed measurement. Another advanced gas evolution analysis involves employing differential electrochemical mass spectrometry (DEMS) based on MS, which

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analyzes gas products from electrode and electrolyte during CV measurements of the EDLC [16]. The DEMS method can be used to obtain results of real-time gas evolution, and the evolution mechanisms can be speculated according to voltage-specific characteristics. However, DEMS should employ a customized electrochemical cell, which provides a different environment than commercial supercapacitor cells. Because the performance and evolved gas in supercapacitors are probably sensitive to cell structure, it is highly recommended that practical supercapacitor cells be directly used for gas analysis.

This study directly used commercial supercapacitor cells for analyzing gas evolution from solvent decomposition at elevated voltage and temperature. To avoid disruption due to gas sampling, which is inevitable, in GC-MS or DEMS, an optical method (Raman spectroscopy) was employed to measure partial pressures of the evolved gases. A nondisruptive analytical setup was then prepared. As long as optical access to the internal volume of a supercapacitor cell is granted, the partial pressures can be monitored indefinitely without actually extracting any gas from the cell. The prepared device was the nondisruptive in situ Raman analysis for gas evolution setup. This analytical setup was used to monitor the partial pressures of evolved gases in an EDLC cell for a highly extended period of 500 h, without affecting the EDLC cell performance significantly. To verify the effect of the Raman cell on gas evolution measurement, its cell performance was compared with the electrochemical performance of an identical commercial supercapacitor cell using various electrochemical analysis methods, such as CV, galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS).

2. Experimental

In our experiment, we tested a cylindrical commercial EDLC (JUWT1475MPD, Nichicon, Rated voltage 2.7 V and rated capacitance 4.75 F) based on a PC electrolyte. Fig. 1 depicts the Raman cell, minimizing gas leakages and dead volume. To seal the Raman cell soft metal was utilized. The dead volume of the Raman cell, which is the sum of the gas collector channel and transfer port, and the internal volume of the commercial EDLC, which was as low as 3.44% of the EDLC volume, were calculated. To avoid gas leakages while allowing the laser access to obtain the Raman signal, thin glass windows were used to seal the top and bottom of the cell body. A hole was created in the bottom center of the commercial EDLC Al case by using a microdrill. The EDLC was then connected and sealed on the cell body's right side. The evolved gas was collected in the gas collector channel. All of these assembly processes of Raman cell were conducted at room temperature, and the relative humidity was maintained at 40%. To minimize any negative influence due to the exposure to air, the Raman cell was assembled in less than 1 min after the hole was drilled. However, it is recommended that the cell would be assembled in argon filled glove box for less exposure to the air. The electrochemical data of the Raman cell showed that the brief exposure to air had no significant effect on cell life and performance compared to those of a control cell.

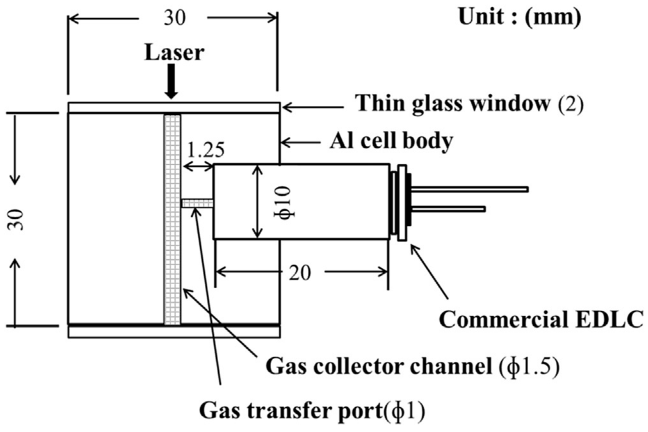

Fig. 1. Schematic representation of the Raman cell used for in situ Raman measurements.

An aging test of the assembled EDLC was performed at a voltage of 2.8 ± 0.02 V by using D.C. power supply (RDP-303AU) in a temperature chamber maintaining 70 ± 1 °C for 500 h. The applied voltage was higher than recommended operating condition (2.7 V) to accelerate the gas evolution from the cell. The Raman signal from the Raman cell was obtained using a commercial micro-Raman instrument (XperRam200. Nanobase.inc) equipped with a 532 nm excitation wavelength. The laser power was set at 108 mW on the cell, and the exposure time was set at 10 s. Before each measurement session, the Raman cell was stored at room temperature for 10 min. For each measurement, we obtained 50 spectra and calculated their average. After the Raman measurements and electrochemical tests, the Raman gas cell was stored again in the temperature chamber.

The electrochemical performance of the EDLCs was analyzed with IviumStat, Ivium technology. The CV was operated at a scan rate of 25 $\mathrm{mV^{-1}}$ to show the typical box shape of EDLCs, and capacitances of the devices were derived by dividing the voltage responsive current by scan rate. The constant current test was conducted 4 times at 200 mA to minimize cell damage from this test. Furthermore, an equivalent series resistance (ESR) was derived from the voltage drop inspired by Electric vehicle capacitor test procedures manual and product guide of Maxwell Technologies® for BOOSTCAP® Ultracapacitors [17,18]. A.C.-impedance spectra were recorded at 0 V and 10 mV magnitudes at frequencies from 0.05 to 100 Hz.

3. Results and Discussion

On the basis of the increasing storage time, the commercial supercapacitor cell performance with the Raman cell was compared to that of the cell without the Raman setup (reference cell). Their CV profiles recorded at 25 $\mathrm{mV^{-1}}$ are plotted in Fig. 2(a). Here, the solid and dashed lines represent the CV curves of the reference and Raman cells, respectively. In this plot, the cell capacitance was calculated by dividing the current by scan rate. The patterns of capacitance (*vs.* potential) are nearly identical for both cells, irrespective of the storage time. Furthermore, cell capacitance reduces (capacitance loss) with the increase in the storage time, which was commonly observed for both cells. Fig. 2(b) displays capacitance retention with increasing storage time, which was obtained by integrating CV curves in Fig. 2(a). Normally, criteria of the end of life are defined at 20% capacitance loss [12]. Therefore, the retention rate of the two cells was highly similar (Difference: ~1%) until the end of life.

Fig. 3(a) shows the charge/discharge profiles of the constant current test. At the middle of the charge/discharge process, the current was cut off to obtain a voltage drop, which can be used for the estimation of ESR. This method was inspired from the methods from the manual and the product guide [17,18]. The current cut-off was maintained for 10 s, and the current was then reversed for 15 s: this step was to ensure accurate ESR measurement. According to this procedure, ESR values for the reference and Raman cells were recorded and are compared in Fig. 3(b). Also, this test was conducted for 3 times on each single cell (Reference and Raman cell) and the results were expressed as dots and error bars. In this figure, the ESR values for individual cells are similar until the eighth day of storage; however, the ESR of the Raman cell is higher