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7. Material Development of Electric Double Layer Capacitor for Fuel Cell Electric Vehicle and the Newly Developed Electric Double Layer Capacitor

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Asahi Glass Co., Ltd. (AGC) and Honda R&D Co., Ltd. have jointly developed a new electric double layer capacitor (EDLC) as an energy storage device for fuel cell vehicles. This EDLC has been utilized in the Honda FCX fuel cell vehicle marketed in December 2002. The Honda FCX fuel cell vehicle required an EDLC with high reliability, high imput / output power and high energy density. The newly developed materials such as electrode, electrolyte and separator realized high. AGC has been continuing the development of better performance EDLC. The performances of recent AGC ultra-capacitor prototypes constructed with newly developed materials and a new capacitor modules composed of the prototypes are descrbed.

1. Introduction

AGC has amassed a host of technology related to electrochemistry since the foundation of electrolytic technology, which is in-house manufacture of caustic soda, using brine electrolysis. With this technological background, AGC was embarked on the development in 1985 of electric double-layer capacitors together with ELNA Co., Ltd., affiliated company of AGC. This cooperative R&D effort led to the commercialization of a small, coin-shaped capacitor used mainly for the back-up power supply of IC memories(1),(2),(3). A subsequent development aimed at applications for high-output power supplies has been continued. AGC and Honda R&D started developing new large-size and high-capacitance EDLC for the hybrid electric vehicles in 1997. But the EDLC at that time had a defect that its energy density was too small to use as an energy storage device for the hybrid electric vehicles. So all the materials that construct the EDLC and the cell structure were reexamined to increase its energy density. The new high-energy capacitors using the newly developed materials, such as electrode, electrolyte and separator, were loaded into the Honda FCX fuel cell vehicle as an energy storage device(4).

Further efforts to improve the cell performance have been continued at AGC. It developed a cylindrical type cell with original structure(5) and the EDLC modules composed of these new cells.

2. Material

2.1 Electrolyte Salt

The requirements placed on the electrolyte were that it should perform high double layer capacitance, and possess high ionic density to ensure high power output, and high usable voltage to enable the system to operate stably at high voltages. In addition, it was desirable for the system to operate at high ionic density to enable safe and stable operation in wide range of temperatures without lack of ion at charge state. Various combination of cations, anions and solvents were tested to find the optimum electrolyte to meet these requirements.

From a view point of electrochemical stability, HOMO, LUMO are calculated for some kind of onium cation and anion by quantum chemical Ab initio (MO) theory and ionic radius are shown in **Tables 1**. Ion size is the rule factor of the thickness of a double layer, and it is reported that the double

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Table 1 Ion Radius, LUMO and HOMO Calculated by Quantum Chemical Ab initio MO. (Gaussian 98, HF76-31G*)

Ions	Ion radius (nm)	LUMO (eV)	HOMO (eV)	Remarks
Me_3EtN^+	0.322	0.69	—	
$MeEt_3N^+$	0.357	1.27	—	Stable, high conductivity
Et_4N^+	0.371	1.25	—	Low solubility
Pr_4N^+	0.444	1.62	—	Low conductivity
EMI^+	0.340	−0.43	—	Not stable to reduction
BF_4^-	0.229	—	−9.5	Stable, high conductivity
ClO_4^-	0.237	—	−7.4	Explosive
PF_6^-	0.254	—	−10.7	Not stable to residual H_2O
$CF_3SO_3^-$	0.270	—	−2.8	Not stable to oxidation
$(CF_3SO_2)_2N^-$	0.368	—	−5.2	Not stable to oxidation

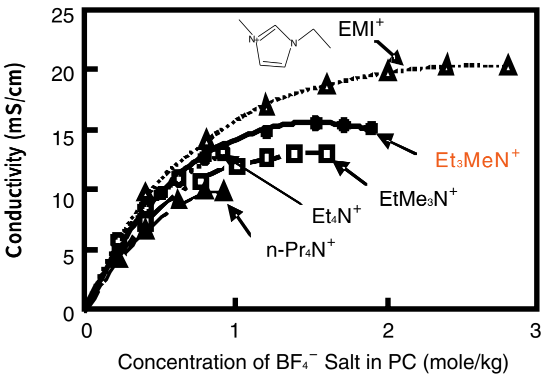


Fig. 1 Conductivities and solubilities of quaternary ammonium tetrafluoroborate salts in propylene carbonate.

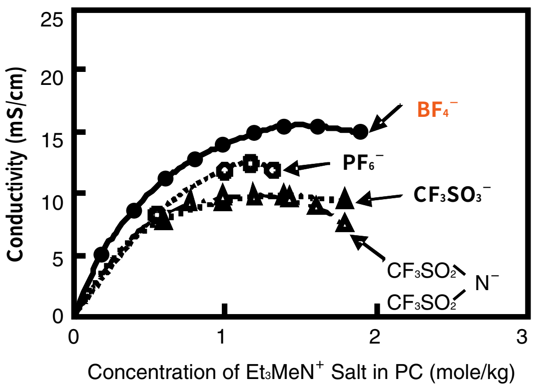


Fig. 2 Conductivities and solubilities of triethylmethyl ammonium salts in propylene carbonate.

layer capacity per unit area is so large that the diameter of ion is small[3]. Moreover, a LUMO value is a measure of stability for oxidation and HOMO value is a measure of stability for reduction. The concentration dependence of the conductivity on the saturation solubility of BF_4^- salt of various cations is shown in **Fig. 1**. The quaternary ammonium cations generally shows lower conductivity than imidazolium salt. But, the quaternary ammonium cation is more stable in reduction.

Generally speaking, the conductivity becomes low, although stability against reduction will become strong, if the ammonium salt has large size alkyl substitution group. Et_3MeN^+ has the character for the best balance in respect of the conductivity, solubility, and stability of reduction.

The concentration dependence of the conductivity up to the saturation solubility of Et_3MeN^+ salt with various anion is shown in **Fig. 2**. BF_4^- and PF_6^- are more stable against oxidation than the other anions. BF_4^- has the best characteristics concerning the hydrolysis stability by moisture, ion size, conductivity, and solubility.

These results led to the selection of Et_3MeNBF_4 as the optimum electrolyte salt[6].

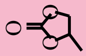
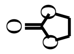
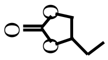
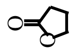
2.2 Electrolyte Solvent

The properties required of the solvent in which the electrolyte salt is dissolved are electrochemical stability (reduction and oxidation resistance as calculated from LUMO and HOMO), high stability of salts, and high conductivity at a wide range of fluid temperatures (freezing and boiling points). These characteristic values are summarized in **Table 2** about the typical solvent used for the electrochemical applications.

The relation between the concentration of the salt and the conductivity of the solutions that contain these solvents up to the saturation solubility of Et_3MeNBF_4 is shown in **Fig. 3**.

AN demonstrates excellent conductivity, but its low boiling point means that vapor pressure would be high in hot environments, indicating potential safety issues. PC was selected as the most suitable solvent, based on a comprehensive consideration taking in electrochemical stability, conductivity, and performance at low temperature and safety.

Table 2 Properties of Organic Solvents Used for the Electrolyte Solutions.

Solvent	Structure	Dielectric constant	Viscosity c.p.	b.p. ℃	m.p. ℃	HOMO eV	LUMO eV	Remarks
PC		65	2.5	242	−49	−12.54	5.80	Stable, High conductivity
EC		90 (40℃)	1.9 (40℃)	238	37	−12.68	5.61	High m.p.
BC		53	3.2	240	−53	−12.48	5.84	Low conductivity
GBL		42	1.7	204	−44	−11.72	5.16	Low Voltage
AN	—≡N	36	0.3	82	−49	−12.63	5.76	Low b.p., Safety Issue
SL		43 (30℃)	10.0 (30℃)	287	28	−11.37	5.87	High m.p.

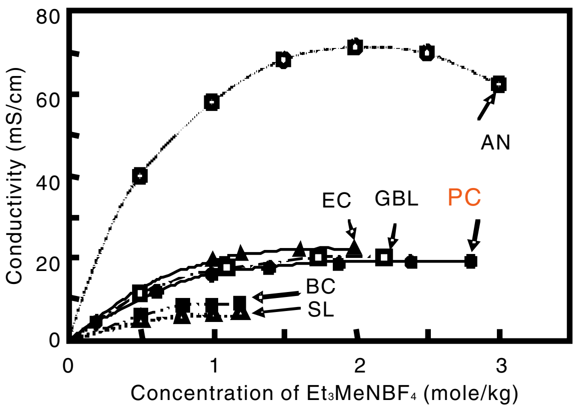


Fig. 3 Conductivities and solubilities of triethylmethyl ammonium tetrafluoroborate in various solvents.

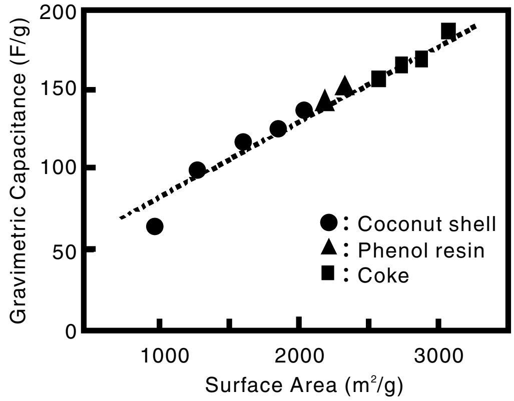


Fig. 4 Correlation between gravimetric capacitance and surface area of activated carbon.

2.3 Separator

Given the possibility of decreasing the thickness, thin film paper formed from synthetic cellulose fiber was utilized for the separator. This separator has the advantages of electrolyte retention, ion conductivity resistance, robustness with respect to handling, wettability and cost[7][8]. This type separator offered the EDLC excellent self-discharge performance.

2.4 Electrode Material

Electrode materials are required to have high capacitance and to be inert against the electrolyte under the condition of high voltage application. Various materials, including activated carbon obtained were tested from these perspectives. It is shown in **Fig. 4** as expected from the charge storage principle to the electric double layer, the gravimetric capacitance increases linearly with the increase in the surface area. **Figure 5** shows the relationship between volumetric capacitance of the electrode and surface area of the activated carbon.

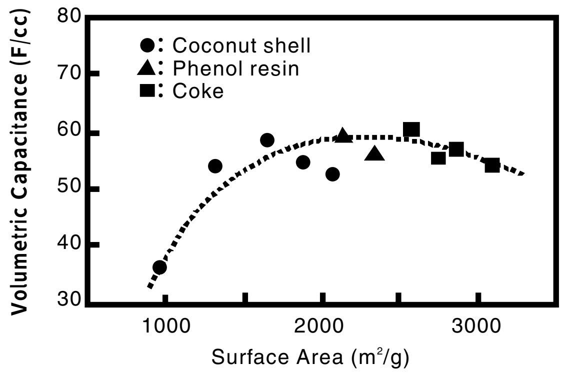


Fig. 5 Correlation between volumetric capacitance of activated carbon electrode and suface area of the activated carbon.

The volumetric capacitance that determines the energy density of the capacitor shows its maximum at the surface area of 2000 - 2500m^2/g, and decreases as the surface area increases over 2500m^2/g. As shown in **Fig.6**, as the specific surface area increases, the pore volume of activated carbon increases and the apparent density of the electrode decreases. As the volumetric capacitance is the

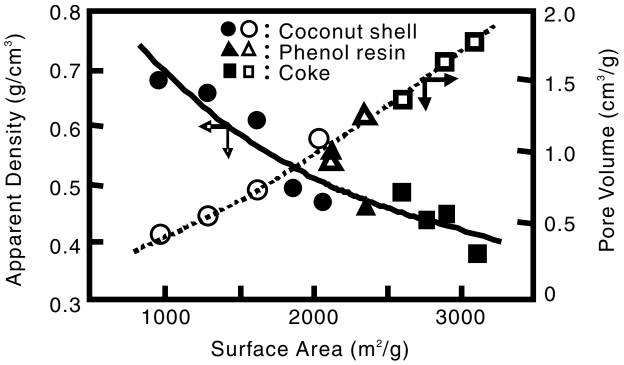


Fig. 6 Correlation between apparent density of PTFE-bonded activated carbon electrode and surface area of the activated carbon.

function of the apparent density and the surface area, the maximum volumetric capacitance is attained by the compromise of the increase in the surface area and the decrease in the apparent density.

On the other hand, the gravimetric capacitance increases linearly with the increase in the surface area. These facts suggest that the double layer capacitance of the kind of carbon species and the pore structure of activated carbon.

It is known that the electrochemical decomposition of electrolyte solvent is strongly related to the existence of oxygen-containing functional groups such as carboxylic and quinine groups on the activated carbon surface[3]. As shown in **Fig.7**, then, the relation between the oxygen content in activated carbon and the capacitance change at the time of voltage application was investigated as one measure of the amount of functional groups containing an oxygen element. These facts suggest that the

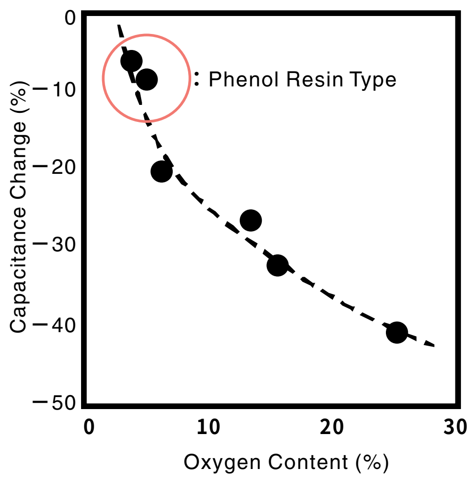


Fig. 7 Influence of oxygen content of activated carbon used for electrode on capacitance change of capacitor after voltage application of 2.8V at 70℃ for 1000h.

removal of the functional groups from the surface of activated carbon is effective to obtain the performances stability of the capacitor during voltage application.

This comprehensive perspective led to the selection of a high-purity activated charcoal as the electrode material. The charcoal has few functional groups, and is formed from a phenol resin with approximately 2000m^2/g obtained by steam activation. Such main materials were adopted into the electric double layer capacitor installed in the FCX.

3. The Newly Developed AGC's Electric Double Layer Capacitor Cell

Figure 8 illustrates a cylindrical cell newly developed by AGC. The aluminum metal container and top cover are sealed together by LASER welding. This sealing technique is highly reliable on the point of the prevention of electrolyte leakage and the tolerance to mechanical vibrations in automotive uses.

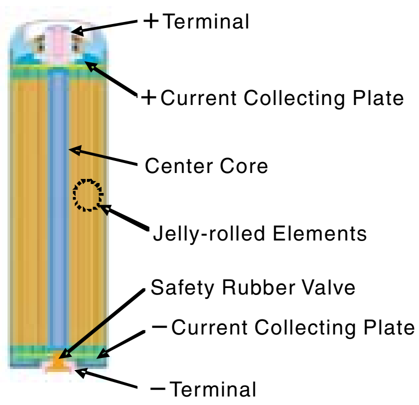


Fig. 8 New cylindrical cell structure.

In conventional cylindrical capacitors or batteries that contain so-called "Jelly-rolled" type elements, "Lead tab" is utilize to connect the electrode with the terminal. We adopt current collecting plates directly connected to the whole edge of the electrode by LASER welding instead of the "Lead tab". This new structure contributes to lowering the internal resistance and also increasing the energy density[9].

A phenol resin type activated carbon activated by steam is the main electrode material, and the electrode is made using the microfibril high-density molding method using fluorocarbon resin PTFE made by AGC[10][11]. These materials and technologies have made it possible to get a high-performance molded electrode with high capacitance density and low electric resistance[(12)(13)]. Those advanced technologies have come to fruition as a new prototype capacitor samples to search new applications. **Table 3** shows the performances of new prototype EDLCs with high nominal voltage 2.7 V and high capacitance.

Table 3 Available Prototype Capacitors.

Type	Dimensions (mm)	Capacitance (F)	Voltage (V)	Internal Resistance (mohm)
DPC05B	D35×L70	550	2.7	7.0
DPC14B	D40×L120	1450	2.7	2.5
DPC20B	D45×L120	2000	2.7	1.8

Figure 9 shows the constant current charging and discharging profiles of DPC14B capacitor between the cut-off voltage of 1V and 2.7V at room temperature. It is clear that the capacitor can be fully charged within 40 seconds in case of constant current of 50A. The horizontal axis shows the product of discharging time and discharging current, which is equivalent coulomb. As can be seen, this capacitor may be discharged at currents of 100A or more, without remarkable iR drop. **Figure 10** shows temperature dependence on the discharge of DPC14B capacitor. At a small current of 10A discharging, gave no changing discharging curves in the temperature range from −30 to 45℃. However, at a higher current of 50A discharging,

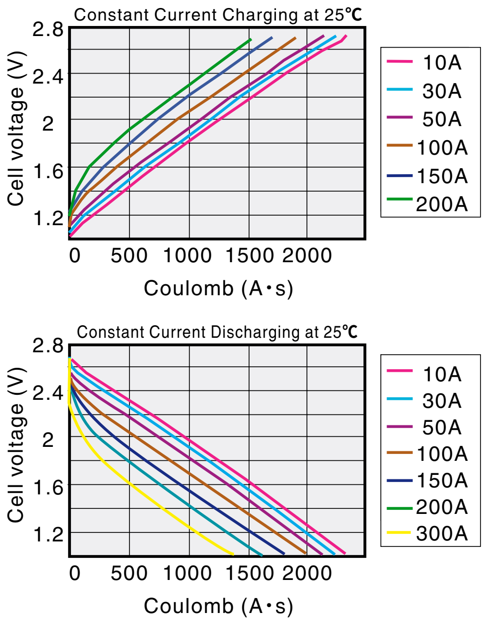


Fig. 9 Constant current charge-discharge characteristics of DPC14B cell.

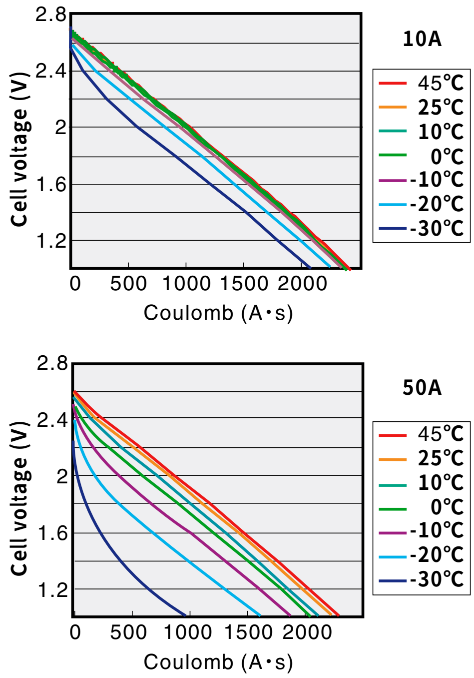


Fig. 10 Temperature dependence on discharge of DPC14B cell.

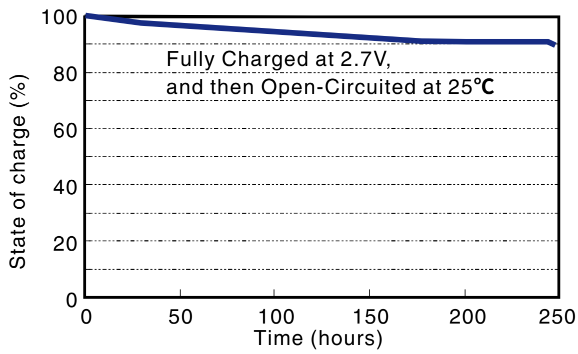


Fig. 11 Self-discharge performance of DPC14B cell.

cell voltages tend to be lower obviously at temperatures below −20℃. These results are mainly caused by the decrease of the conductivity of Et_3MeNBF_4/PC electrolyte at low temperatures. The self-discharging performance is shown in **Fig.11**. The charge loss of the capacitor after 10 days at room temperature is within 10%, which is almost the same level as that of Ni-hydrogen battery.

4. AGC's Capacitor Module

For automotive applications that require high voltage operation, AGC has also developed a new capacitor module composed of number of cells connected in series. **Figure 12** shows an outside view of a 42V-80F capacitor module and its specifications. This module comprises 18 cells of DPC14B connected in series and is equipped with an individual cell-voltage balancing circuit [14]. And the module is composed of three units that have six cells in series per unit, so it is easy to obtain the higher voltage module by installing more units.

Specifications
- Theoretical energy : 19.6Wh (42V-0V)
- Energy Density : 3.6Wh/L
- Rated Voltage : 42V
- Surge Voltage : 50V
- Capacitance : 80F
- Internal Resistance : 50mohm
- Dimensions : 265×135×152mm
- Volume : 5.4L
- Weight : 6.1kg
- Number of Cells : 18 cells in series

Fig. 12 42V-80F capacitor module ACTC 4012-6M3.

We believe this capacitor module attains the highest energy density. The theoretical energy density of the module achieves to 3.6Wh/L.

Figure 13 shows the constant current charging and discharging characteristics of ACTC4012-6M3 capacitor module between the cut-off voltage of 21V and the rated voltage of 42V at room temperature. It was found that the module could be discharge at 100A without a large performance drop. It indicates that we can operate the module at about 3kW.

Figure 14 shows temperature dependence on charge-discharge characteristics of ACTC4012-6M3 module.

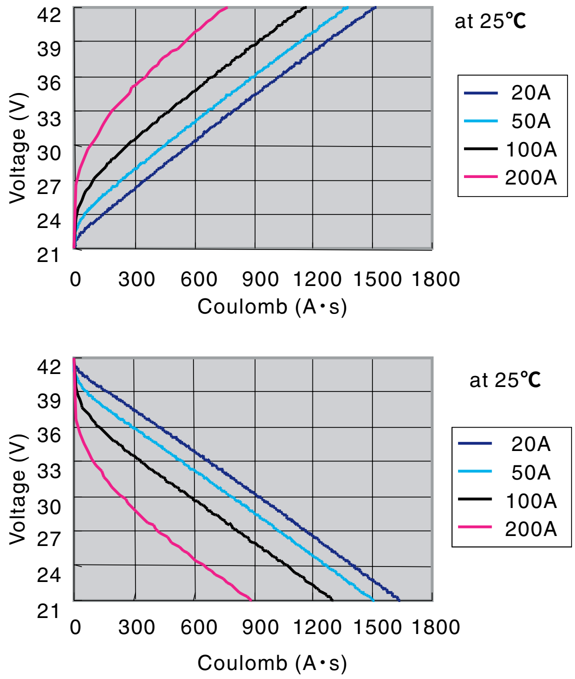


Fig. 13 Constant current charge - discharge characteristics of ACTC4012-6M3 module.

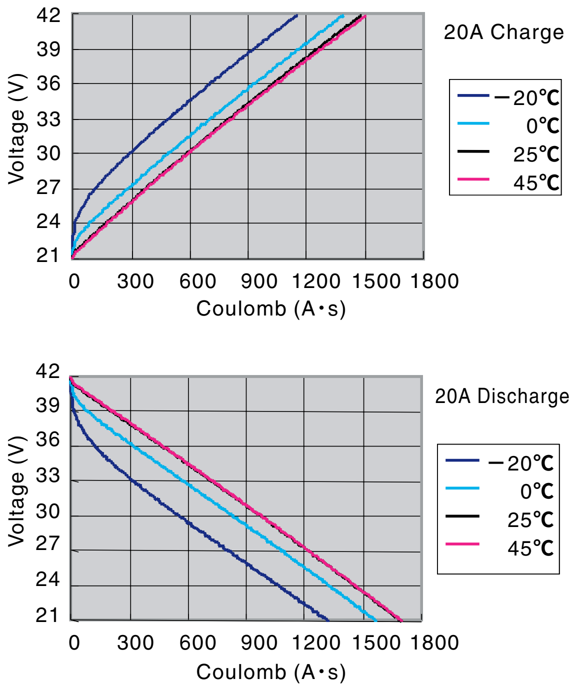


Fig. 14 Temperature dependence on charge-discharge characteristics of ACTC4012-6M3 module.

It was confirmed that this module could work even at −20°C. Above-mentioned performances of the capacitor module were roughly consistent with the expected values calculated from the performances of the single cell.

5. Conclusion

It is a first time in the world that an electric double layer capacitor system has been utilized as an energy storage system in a passenger vehicle, the Honda FCX fuel cell vehicle. The capacitors were developed to perfectly match the performance requirements of the FC system, with both cell configuration and functional materials studied to improve cell performance. From the perspective of functional materials, the system is features by a newly developed high-capacitance activated carbon and an electrolyte which is safe and performs in a wide range of operating temperatures, enabling it to be used in an automotive application. In addition, the unit cylindrical cell with original structure and the module of EDLC were developed using these developed material in Asahi Glass CO., Ltd. to search new applications.

−Acknowledgments−

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