Development of Electrically Conductive DLC Coated Aluminum Substrate for the Advanced Electric Storage Devices by Plasma Ion Assisted Deposition Method

Masayasu Tanjyo
Nakagawara 34-1, Kamitoba Minami-ku Kyoto Kyoto, 601-8142 JAPAN
m.tanjo@plasma-ion.co.jp

Yasuo Suzuki
Nakagawara 34-1, Kamitoba Minami-ku Kyoto Kyoto, 601-8142 JAPAN
y.suzuki@plasma-ion.co.jp

Abstract—This paper relates to the development of electrically conductive DLC coated Aluminum (Al) substrate for the advanced electric storage devices by Plasma Ion Assisted Deposition (PIAD) method. Due to its low contact resistance and high corrosion resistance capability the electrically conductive DLC coated Al substrate is confirmed to be useful as the electrode material of the electric storage devices such as EDLC, LiC, LiB, especially for the increase of the cell voltage.

Keywords—conductive DLC, resistance, corrosion, electric storage device

I. INTRODUCTION

A. Diamond like Carbon Material

A diamond-like carbon (DLC) film is a material positioned between diamond and graphite. When DLC is coated on the surface of the steel material, the coefficient of friction is reduced to 1/4 and the abrasion resistance is dramatically improved. In addition, the amorphous DLC film containing hydrogen has toughness, and when coated on plastics, it has the property of not passing oxygen and water. Utilizing these characteristics, the application market as a low friction / wear-resistant member of mechanical materials, tools and electronic devices, and as a gas barrier coating of PET bottle is greatly expanding. Since the raw material is carbon, it has environmental harmony, and the scope of application of DLC seems to expand further in the future.

On the other hand, as shown in the application for the electrostatic protection or electrical contact material, DLC also have the electrical property and is used in the electrical field. However, it does not look like it is tightening a big market on an industrial scale.

We have been promoting development of electrically conductive DLC for a fuel cell separator [1]. And we have verified the possibility of reducing the resistance and improving the corrosion resistance by depositing electrically conductive DLC on the Al substrate as the electrode of the electric storage device, under support of AIST [2]-[6]. As is well-known, this market is widespread today.

B. Electric Storage Device & its Market

Recently, the new electric storage devices which equips on the Electric Vehicles (EV), Electric Double Layer Capacitor (EDLC), Lithium Ion Capacitor (LiC), Lithium Ion Battery (LiB) were developed. Fig. 1 compares those device’s power density (W/kg) and energy density (Wh/kg) per kg. Depending on the electrode materials, LiC has a high power density and the high instantaneous current, and LiB has a high energy density and the long operation life time. EDLC has an intermediate performance of them [7]. Among them, LiB has the largest market size, which is divided into the mobile phone battery, the stationary power battery, and the automotive battery. The automotive battery market is the biggest now and the highly rise rate.

In TABLE I it is shown the main compositions of the positive / negative electrode, separator and electrolyte of the electric storage devices. Since EDLC does not use the reactive lithium, it can be said the most secure.

### TABLE I. ELECTRIC STORAGE DEVICES: STRUCTURE OF EDLC, LiC, LiB

| Electric Storage Devices | Negative Electrode | Positive Electrode | Separator | Electrolyte |
|--------------------------|--------------------|--------------------|-----------|-------------|
| EDLC                     | Activated carbon   | Activated carbon   | Insulation films | NaPF6-in Dimethoxyethane (DME) |
| LiC                      | Carbon             | Activated carbon   | Insulation films | non-aqueous LiPF6 etc. |
| LiB                      | Carbon, LTO etc    | Lithium oxide, LiNiCoMnO2 | Nonwoven fibers, polymer films | non-aqueous LiPF6 etc. |
In Fig. 2, it shows the trends in market size of each constituent electrode material. The total market size of 10.2 B $ in 2016 has doubled to 22.5 B $ in 2020, which shows that it is growing at a rate of 17% per year. It is said that it will further expand after 2020. Expansion of the market size as described above constitutes the front and back of the technology development of the product, and it is necessary to achieve the main theme for improvement of the electric storage device.

II. METHOD AND EQUIPMENT

A. PBIID vs. PIAD deposition method

There are some kinds of DLC film formation methods, one is the arc-ion plating another is the sputtering. But those films are basically porous because DLC film consists of large size carbon particles. Therefore it cannot be avoided to be inferior to corrosion resistance. In method of developed PBIID [2]-[6] technology (Plasma Based Ion Implantation and Deposition), which ionizes the Hydrocarbon mixture gas by applying RF and high pulsed voltage, the carbon ion is implanted and deposited on the substrate, and electrically conductive DLC film is formed. This film is porous free and superior to corrosion resistance.

On the other hand, PBIID has two methods, CCP (Capacitively Coupled Plasma) and ICP (Inductively Coupled Plasma). Fig. 3 shows comparison of two methods. Feature of ICP method is that plasma density is very high and deposition rate is very fast. The Hydrocarbon mixture gas is ionized and applying RF and high pulsed voltage, carbon ion is implanted and deposited to substrate, and electrically conductive DLC film is formed, which is called PIAD (Plasma Ion Assisted Deposition) method.

| No. | PBIID | PIAD |
|-----|-------|------|
| Plasma | Antenna method (13.56M-CCP) | 13.56M-ICP |
| RF-Power source structure | Flat plate/Cylindrical mesh | One turn coil |
| Plasma density | ~3E10/cm³ | ~3E11/cm³ |
| Plasma uniformity | ±10% | ±10% |
| Deposition Speed | 1μm/hr | 5μm/hr(*) |

*The RF power: 3kW

B. R to R DLC Coating System

In Fig. 4, it is shown the Roll to Roll coating system which makes high throughput with both-sides PIAD plasma coating. The aluminum substrate roll is set on the above vacuum chamber and flows into the plasma processing chamber with heating and then the substrate is rolled up at the below vacuum chamber.
III. DIAGNOSTICS AND MEASURED RESULTS

A. Contact Resistivity

The contact resistance has a unit of Ωcm² as a physical quantity obtained by converting the potential difference when electric current passes through the surface touched by a dissimilar substance into resistance. Since the contact surface in usually is not flat that the contact area is smaller than apparent, and the current density in the contact surface is actually large. The contact resistance is a resistance value considering the effective contact surface and can be evaluated by the heat generation $W = I^2 R_s$ at the contact-surface.

In the case of an electric storage device, since the contact resistance between the DLC film formed on aluminum and the electrode active material is the object, evaluation is made by direct contact resistance between the case where the carbon paper (GDL), as substitution of activated carbon, is sandwiched and the gold, which are shown in Fig. 5.

![Fig. 5. Contact resistivity measurement](image)

B. Contact Resistivity vs. Heater Temperature

In Fig. 6 it is shown the typical result of contact resistivity vs. heat temperature at the experimental conditions. It is shown the high temperature makes low resistivity.

![Fig. 6. Contact resistivity and heater temperature](image)

| No | 1  | 2  | 3  |
|----|----|----|----|
| Heater Temperature (°C) | 200 | 300 | 400 |
| $R_{sg}$ (mΩcm²) | 292 | 134 | 70.9 |
| $R_{sa}$ (mΩcm²) | 6.4 | 0.407 | 0.215 |

Even in the severe corrosion resistance test in concentrated sulfuric acid, compared with the uncoated substrate leak current of 2E-4A/cm², the coated one is 7E-7 A/cm² at 0.65V at the typical operation condition. Only a very weak current of about 1/300 or less flows. It is understood that the electrically conductive DLC film has a high denseness and is excellent in the conductivity as well as the corrosion resistance.

C. Corrosion Resistivity and Leak Current

In Fig. 7, it is shown the anodic polarization curve with electrically conductive DLC for Al substrate.

![Fig. 7. Leak current measurement of DLC film for Al substrate](image)

D. Hydrophilicity

Fig. 8 shows the results of evaluating the property of imparting hydrophilicity by plasma treatment after DLC coated Al film with a contact angle. Without the treatment, the contact angle is around 70 degrees, indicating hydrophobicity, but it shows hydrophilicity at a contact angle of 30 degrees or less by the treatment for about 2 minutes. The adhesion of the slurry which consists of the Cell electrode material can be improved, which is effective for the reduction of the Cell circuit resistivity and the repeatability. In the same figure it is shown the hydrophilicity after treatment time variation.
Fig. 8. Surface treatment by O2 for hydrophilicity control, gives surface hydrophilicity which makes high contact of slurry of activated carbon.

IV. ELECTRIC STORAGE CELL EVALUATION

A. Cell Impedance and Rate Discharge Test

It shows in Fig. 9, the DLC coated Al cell resistance is 0.3Ω, that of non-coat base Al is 2.4Ω, and that of the usual etched Al is 0.6Ω which is 1/2 lower resistance. After the rate discharge of 500C the rate retention of 88.6% means suitable for the EDLC cell and is expected to be prefer for other electric storage devices.

![Cell Impedance vs Resistance](image)

B. Withstand Voltage Test by DLC coated EDLC Cell

EDLC Cell for evaluation test conditions are as follows, the substrate; 400°C DLC coat Al substrate.

1) Withstand voltage test by EDLC Cell

2) Leak current test: Test temp.: 60 degC Applied voltage: 2.7V→2.9V→3.1V→3.3V and 3.1V/5 hours charging +100 hours hold voltage.

![Applied voltage & leakage currents](image)

It shows, DLC coated EDLC Cell have a 3.1V and more withstand voltage. As the energy density is direct connecting with the withstand voltage Vws that, 
\[
Ed = kVws^2 = (3.1V / 2.7V)^2 = 1.3
\]

It is expected the energy density increases to 1.3 times.

V. CONCLUSIONS

- Electric storage device such as LiB, LiC, EDLC recently with big expand for the market of the EV, which requires high energy, high current, high safety and low cost.
- Experimental results of electrically conductive DLC of PIAD applied to the EDLC cell shows higher operation voltage of 2.7V to 3.1V, higher corrosion resistivity of leakage current 2E-4A/cm² to 7E-7A/cm², and lower circuit resistance of 0.6Ω to 0.3Ω.

- Requirement of the electric device of high energy asks high voltage operation with high corrosion resistivity and low circuit resistance, it is confirmed that the electrically conductive DLC of PIAD has the solution potentiality for those requirements.

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