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LiNiO₂ electrode modified by plasma chemical vapor deposition for higher voltage performance

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Abstract

Surface modification of the electrode improved the performance of the LiNiO₂ electrode charged to 4.6 V. An amorphous carbon thin film was uniformly deposited on the electrode surface using dc plasma chemical vapor deposition. This surface treatment suppressed electrolyte decomposition during the charge process. When a coin-type cell using this electrode was charged to 4.6 V, the charge–discharge efficiency was 84% in the first cycle and 96–98% through the second to fifth cycles. This treatment suggests a new approach to the development of the positive electrode for lithium-ion secondary batteries. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: LiNiO₂; Surface treatment; Plasma CVD; Amorphous carbon; Lithium-ion battery

1. Introduction

Since the early investigations [1], LiNiO₂ has been proposed as a promising positive electrode active material in lithium-ion secondary batteries [2]. Compared with the widely used LiCoO₂, LiNiO₂ is less expensive and has a higher capacity in the conventional charge–discharge conditions [3,4]. In addition to the structural instability during charge–discharge process [5–11], however, the material's reaction with electrolytes is a problem [12–16]. In this study, the surface modification of LiNiO₂ electrode was tried to give a new approach to solve these problems.

We have been studying the surface modification of electrodes for the purpose of suppressing electrolyte decomposition and obtaining better electrode performance [17,18]. Our strategy for surface modification is to treat the formed electrode surface rather than the particles of the electrode material. In the second way the whole particle surface can easily be modified, but the surface modification effects the particle contact, the ease of preparation of the electrode, and the electronic conductivity of the electrode. In the first way, these problems can be avoided but a uniform treatment of all the electrode particles could be difficult. In our previous study [18], plasma chemical vapor deposition (CVD) was performed on the LiCoO₂ electrode to treat the entire

electrode surface easily. Decomposition of the electrolyte solution was suppressed by the plasma CVD film, and the discharge capacity and charge–discharge efficiency of the electrode charged to 4.6 V was drastically improved.

We report here surface modification of the LiNiO₂ electrode surface using dc plasma CVD of ethylene. The modified LiNiO₂ electrode was cycled between 3.0 and 4.6 V in a coin-type cell.

2. Experimental

2.1. Electrode preparation

For the synthesis of LiNiO₂, LiOH·H₂O and Ni(OH)₂ (Wako Pure Chem. Ind., Ltd.) were mixed by stoichiometric ratio and heated to 500°C for 4 h in oxygen. The sample was then cooled, crushed and heated to 740°C for 12 h in oxygen. The prepared LiNiO₂ was mixed with 6% of synthetic graphite (KS-15, Lonza) as the conducting material and 3% of polyvinylidene 1,1-difluoride (PVDF, Aldrich) as the binder, and was pressed with an aluminum mesh to form the pellet electrode.

2.2. Plasma CVD

The formed pellet was put into a vacuum chamber and was positioned on the cathode for dc glow discharge. The

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chamber was then evacuated to less than 10^{-3} Torr and C_2H_4 was introduced at a flow rate of 10 ml/min at standard temperature and pressure (STP). The system pressure was maintained at 0.08 Torr by controlling the needle bulb between the chamber and pumping system. Plasma CVD was carried out by applying dc power of 1.2 kV between the parallel capacity coupled electrodes for 1–5 min.

2.3. Characterization

Scanning electron microscopy (SEM) was carried out using a Hitachi S-4000 microscope. X-ray photoelectron spectroscopy (XPS) was performed using an SSI S-Probe spectrometer. X-ray diffraction (XRD) patterns were measured using an RINT 2500V diffractometer (Rigaku Co.) equipped with a Cu $K\alpha$ radiation source and a diffracted beam monochromator.

2.4. Coin-type cell test

The performance of the pellet electrode was evaluated using a coin-type cell. The test cell was assembled in a 2025 cell with the electrode pellet, a lithium metal counter electrode, a polypropylene separator and the electrolyte solution. The electrolyte solution used was 1 M $LiPF_6$ in 1:1 propylene carbonate (PC) and dimethylcarbonate (DMC) (Tomiyama Pure Chem. Ind., Ltd.). The coin-type cell was assembled in an Argon-filled globe box (Mecaplex, GB82) at oxygen and water concentrations below 5 and 1 ppm, respectively.

The cell was charged galvanostatically up to 4.2 or 4.6 V (versus Li/Li^+) with a current density of 0.25 mA/cm^2 , then charged potentiostatically until the current density decreased below 5 mA/cm^2 . For safety reasons, the total charge time was limited to 36 h, regardless of the potential and current. Discharge was carried out galvanostatically to 3.0 V (versus Li/Li^+) with a current density of 0.25 mA/cm^2 .

3. Results and discussion

3.1. Characterization of plasma CVD film

The deposit on the electrode surface obtained by plasma CVD was first characterized. Fig. 1 shows the SEMs of the electrode pellets before and after plasma CVD. The synthesized $LiNiO_2$ consisted of particles from 10–20 μm . No distinctive morphological change was observed before and after plasma CVD in the micrographs, suggesting uniform coverage of the electrode surface consisting of $LiNiO_2$ particles by plasma CVD.

The electrode surface was then characterized by XPS. Before plasma CVD (Fig. 2a), XPS peaks of Li, Ni, and O from $LiNiO_2$, C and F from the binder, and C from the conducting material were detected from the $LiNiO_2$ elec-

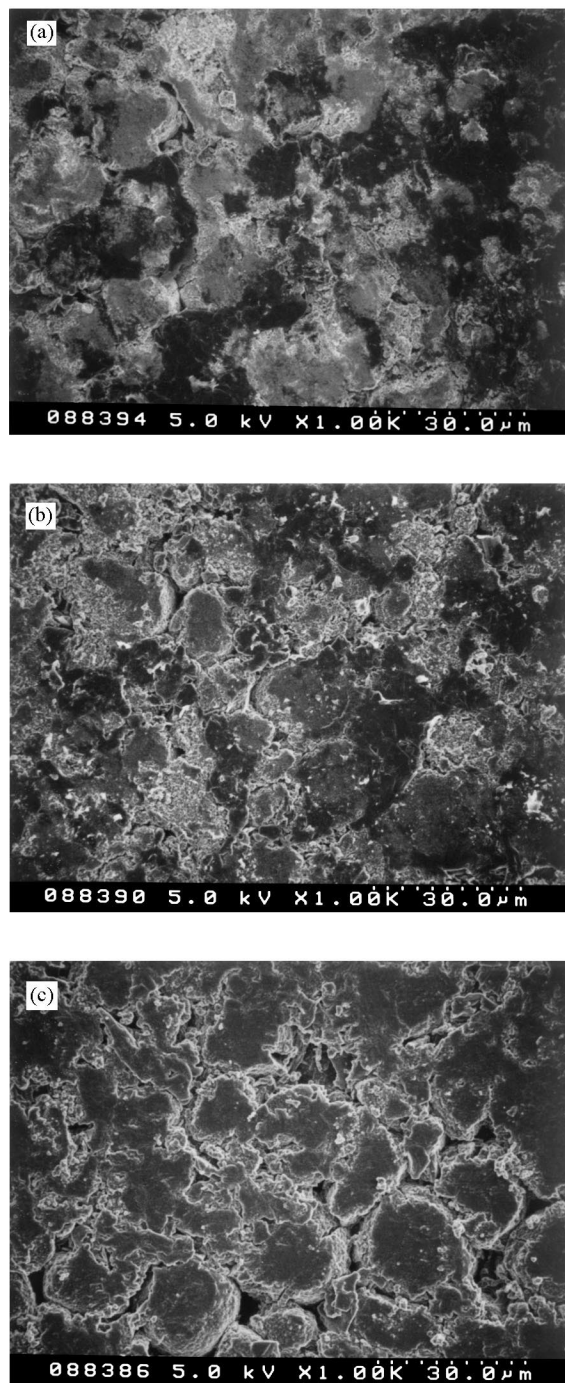


Fig. 1. Scanning electron micrographs of $LiNiO_2$ electrodes after (a) 0; (b) 1; and (c) 3 min of plasma CVD.

trode surface. With the exception of C and O, these elements are not found on the electrode surface after 1 min of plasma CVD (Fig. 2b). This means that the $LiNiO_2$ electrode surface was completely covered with the plasma CVD film, which consists mostly of C and a small amount of O.

Fig. 3 shows C 1s photoelectron spectra for the $LiNiO_2$ electrodes. XPS peaks at 284.5 and 286 eV in Fig. 3a are attributed to C–C bonds. The former peak is from the

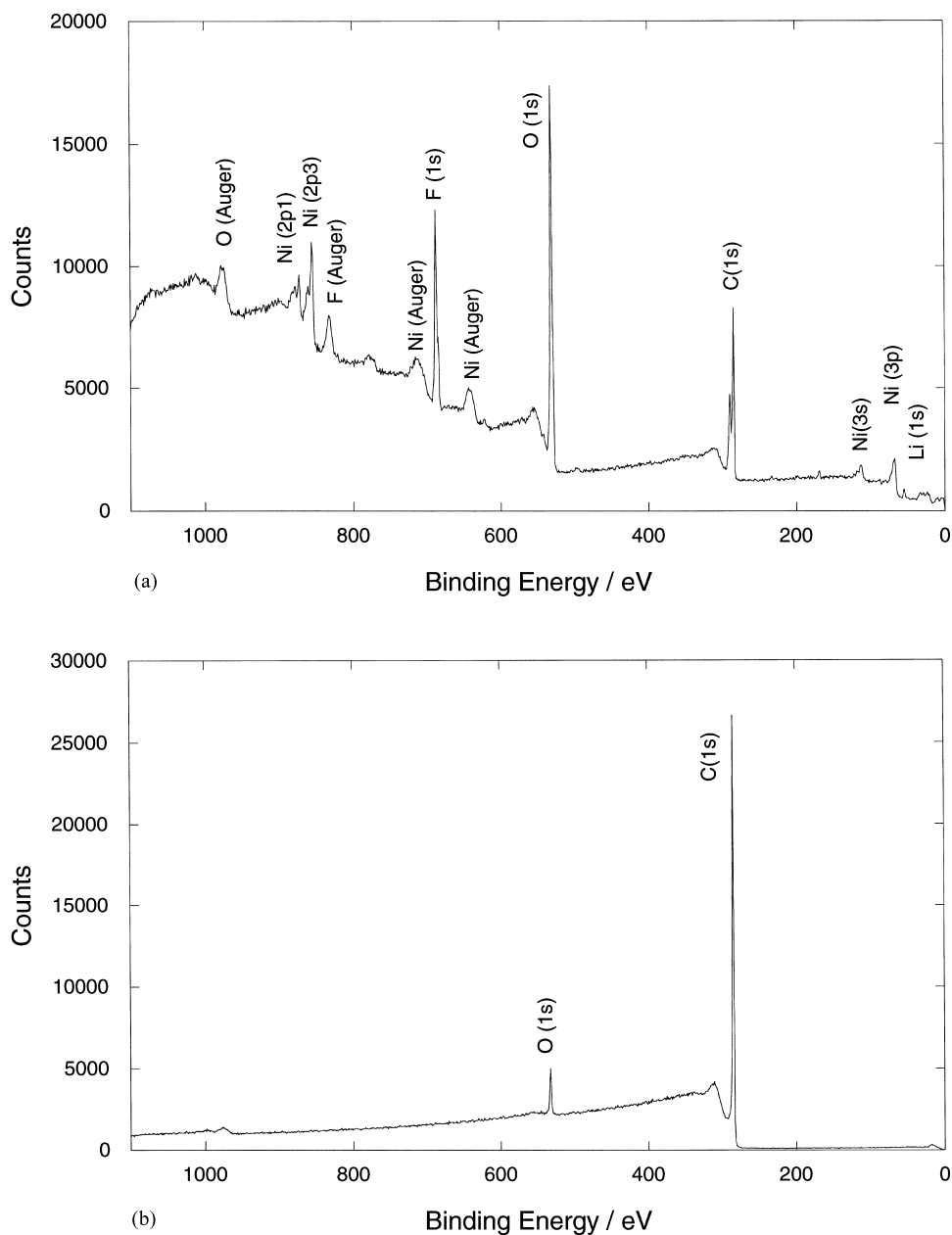


Fig. 2. XPS survey spectra for LiNiO_2 electrodes after (a) 0; and (b) 1 min of plasma CVD.

conducting material and the latter from the binder. Another XPS peak at 290 eV is attributed to C–F bond from the binder. After plasma CVD, the peak at 290 eV disappeared, which is consistent with the disappearance of the fluorine content in Fig. 2b. Further, the peak at 285 eV became broader, suggesting the deposition of a disordered carbon.

The SEM figures and XPS spectra suggest the uniform deposition on and complete coverage of the electrode by the plasma CVD film. The film thickness on the top surface of the electrode was estimated to be about 0.1 μm for 1 min of the plasma CVD.

Fig. 4 shows the XRD pattern of the CVD carbon film. In order to eliminate the peaks from the conducting material of the electrode, a nickel plate was used as the substrate. None

of the characteristic peaks except for those of the nickel plate was observed, so the plasma CVD film is an amorphous carbon. As was discussed in our previous report [18], the structure of the deposit was not significantly affected by the kind of the substrate in this dc plasma CVD, and the Raman spectrum suggested that the carbon film deposited by the dc plasma CVD of ethylene is a diamond-like carbon (DLC).

3.2. Electrode performance

The effect of the plasma CVD film deposited on the LiNiO_2 electrode (with binder and conducting material) on the electrode performance was evaluated using coin-type cells. The impedance of the electrode was not increased by

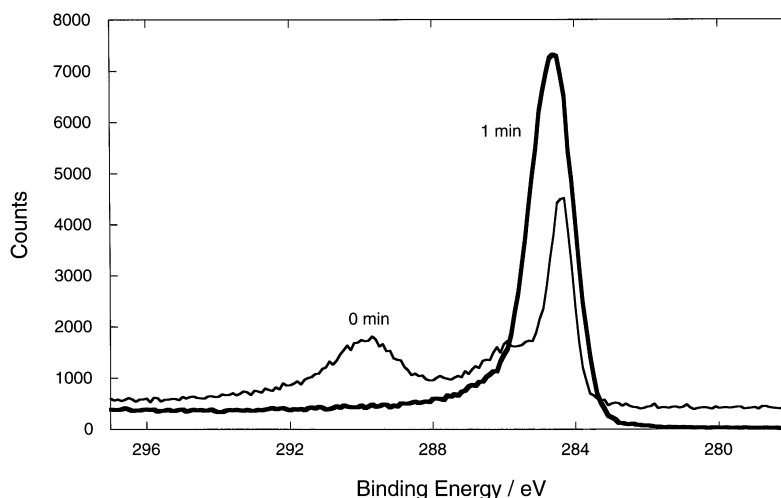
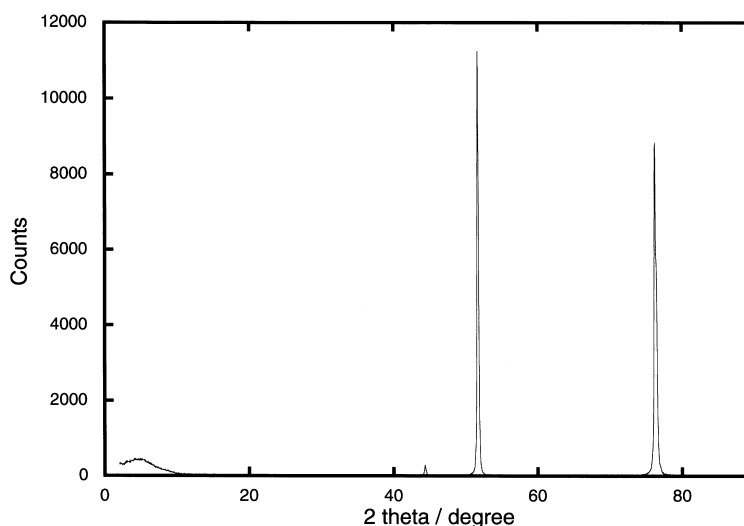
Fig. 3. C1s photoelectron spectra of LiNiO₂ electrodes.

Fig. 4. XRD pattern of plasma CVD film on Ni substrate.

the plasma CVD film. Table 1 shows the electrode performance of the LiNiO₂ electrode charged up to 4.2 V. In spite of its low electronic conductivity, the plasma CVD film did not reduce the discharge capacity or the charge–discharge efficiency.

Fig. 5a shows the charge–discharge curve of the LiNiO₂ electrode without plasma CVD, charged up to 4.6 V. In the charge process over 4.5 V, both the electrode potential and the charge current were unstable. The charge process was

therefore terminated after 36 h. The total charge capacity in the first cycle was 312 mAh/g, which is far beyond the theoretical value of 275 mAh/g. The irreversible capacity of over 130 mAh/g may be attributed to electrolyte decomposition during the charge process.

The performance of the electrode charged up to 4.6 V was greatly improved by plasma CVD, as can be seen in Fig. 5b–d. The thickness of the plasma CVD film did not strongly effect on the charge–discharge curves. The charge curves are monotonic and the charge process was terminated by the threshold current. The charge capacity of the electrode with 3 min of plasma CVD was 250 mAh/g ($x = 0.09$ in Li_xNiO₂). The discharge curves are also monotonic and the discharge capacity was 211 mAh/g with 3 min of plasma CVD. The resulting charge–discharge efficiency was 84.3%, which is higher than that of the 4.2 V charge. The still-remaining irreversible capacity may be intrinsic for the LiNiO₂, although we have not yet confirmed it.

Table 1
Electrode performance of LiNiO₂ electrodes charged up to 4.2 V

Electrode	Discharge capacity (mAhg ⁻¹)	Charge capacity (mAhg ⁻¹)	Efficiency (%)
LiNiO ₂	182.8	226.7	80.6
LiNiO ₂ (plasma-treated)	184.7	225.5	81.9

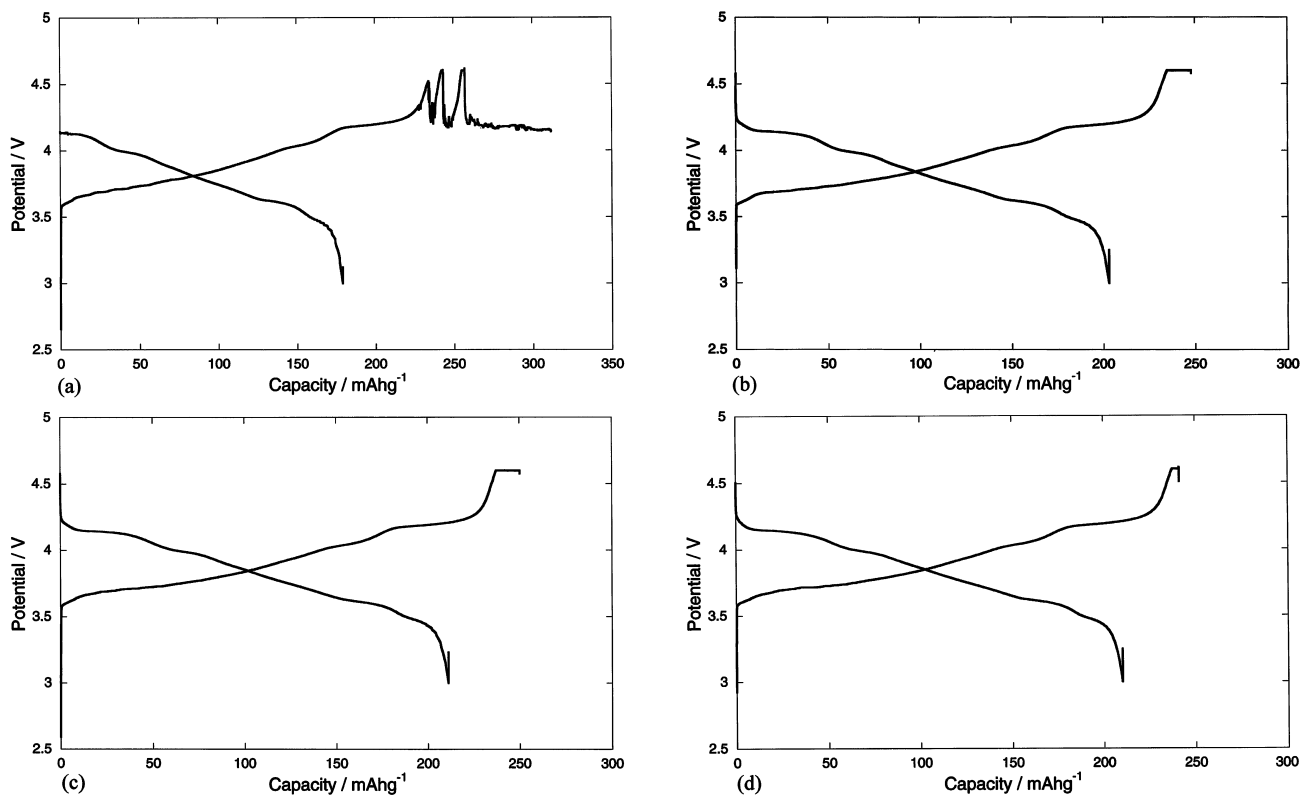


Fig. 5. Charge–discharge curves of LiNiO_2 electrodes with (a) 0; (b) 1; (c) 3; and (d) 5 min of plasma CVD charged up to 4.6 V.

A further significant improvement in electrode performance after plasma CVD is seen in the cycle performance, as shown in Fig. 6. In the electrode without plasma CVD, the charge process was terminated after 36 h in every cycle, since both the potential and current were unstable. The cycle performance in discharge capacity was not reproducible, and the charge–discharge efficiency was under 40% after the second cycle. The irregular change of the discharge capacity may be due to the gas evolution by the electrolyte decomposition. With 3 min of plasma CVD, the cycle performance was almost constant and the charge–discharge efficiency was over 96% after second cycle. The film growth on the surface of the lithium counter electrode and structural changes in the LiNiO_2 electrode materials could cause a slight decrease of the capacities with cycling.

Thus, so far we have seen that the electrolyte decomposition was suppressed by the plasma film and the performance of the electrode was drastically improved when the electrode was charged up to 4.6 V.

We believe that controlling the electrode/electrolyte interface is crucial to the development of lithium-ion secondary batteries including polymer batteries. The irreversible reactions both on the positive and negative electrode surface impair the battery performance. Thus, in addition to further developing the electrode materials themselves, controlling the structure of the electrode interface by surface modification is essential.

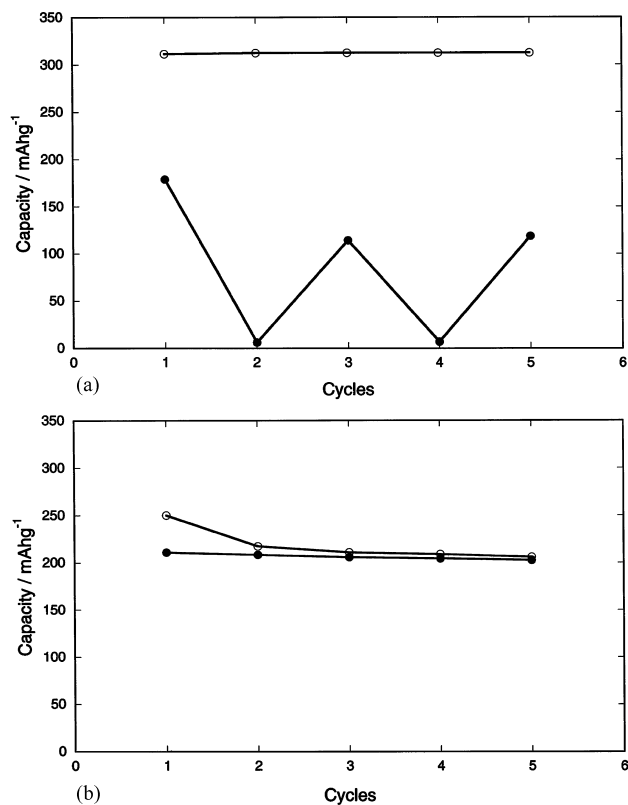


Fig. 6. Charge–discharge capacity of LiNiO_2 electrodes with (a) 0; and (b) 3 min of plasma CVD charged up to 4.6 V. ○: charge capacity and ●: discharge capacity.

4. Conclusion

The LiNiO₂ electrode surface was uniformly covered with plasma film using dc plasma CVD of ethylene. The electrode performance was drastically improved by this surface treatment. The discharge capacity of the first cycle was 211 mAh/g and the charge–discharge efficiency was 84% in the first cycle and 96–98% through the second to fifth cycles, when the electrode was charged up to 4.6 V. This improvement in the electrode performance due to the suppression of the electrolyte decomposition by the plasma film, suggests a new approach to the development of the positive electrode for lithium-ion secondary batteries.

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