



# Analysis of solid electrolyte interface formation reaction and surface deposit of natural graphite negative electrode employing polyacrylic acid as a binder



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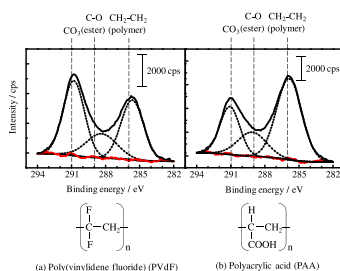
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## HIGHLIGHTS

- The XPS spectra of C1s region for NG-3 electrode after discharging up to 2.0 V is shown.
- The NG-3 electrodes using PAA and PVdF as the binders, respectively are shown.
- The amount of the inorganic components of the SEI was low in the case of the PAA binder.
- The binder types have an influence on the SEI composition.

## GRAPHICAL ABSTRACT



High resolution XPS spectra (—), fitting curves (····), and the error (—)

## ARTICLE INFO

### Article history:

Received 9 April 2013

Received in revised form

8 August 2013

Accepted 21 August 2013

Available online 3 September 2013

### Keywords:

Lithium-ion battery

Natural graphite

Negative electrode

Polyacrylic acid

Binder

Solid electrolyte interface (SEI)

## ABSTRACT

We analyzed the solid electrolyte interface (SEI) formation reaction and surface deposit of a natural graphite (NG-3) electrode employing polyacrylic acid (PAA) as a binder in an ethylene carbonate-based electrolyte because it was reported that the initial charge–discharge characteristics of the NG-3 electrode were improved by employing the PAA binder. Poly(vinylidene fluoride) as a binder was used for comparison. We investigated the influence of the binder types on the coating of the NG-3 particles using the B.E.T. specific surface areas. The difference in the above phenomenon was explained by the relationship between the B.E.T. specific surface area and the irreversible capacity. The surface chemical composition of the NG-3 electrode was investigated by FE-SEM/EDX and XPS and then the difference between the PAA binder and the PVdF binder was discussed. The FE-SEM/EDX and the XPS results showed that the amount of the inorganic components of the SEI was relatively small in the case of the PAA binder NG-3 electrode. The AC impedance results showed that the SEI film resistance of the PAA binder NG-3 electrode was lower at 0.2 V. It was clarified that the binder types affected the coating state, the SEI formation reaction, and the SEI film composition.

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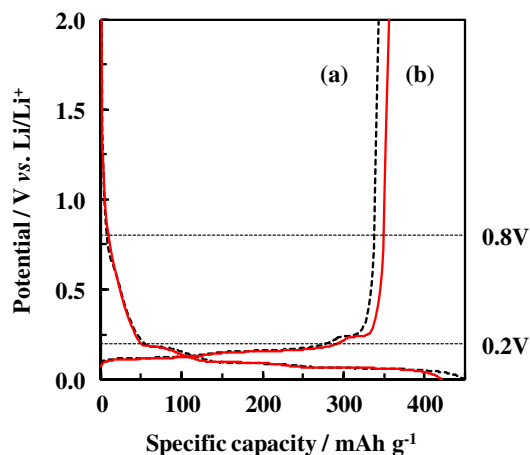
## 1. Introduction

Various improvements in the electrochemical characteristics of the graphite electrode have been reported. As an example, the

initial irreversible capacity of the graphite electrode in an ethylene carbonate (EC)-based electrolyte was reduced by employing gelatin as a binder [1,2]. In addition, the same research group reported that the initial irreversible capacity of the graphite electrode in the EC-based electrolyte was reduced by employing a water-soluble polymer of sodium carboxymethyl cellulose (CMC-Na) as a binder [3]. In recent years, it has been reported that the contact area

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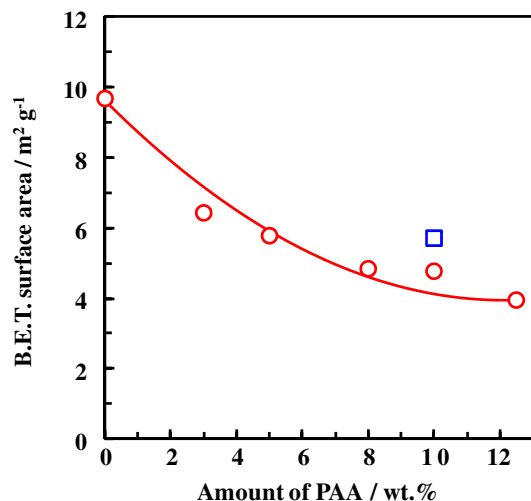


**Fig. 1.** 1st charge–discharge curves of NG-3 electrodes using (a) PVdF 10 wt. % and (b) PAA 10 wt. % as the binders in the  $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{EC} + \text{DEC}$  (50:50 vol. %) electrolyte [5]; potential range: 5 mV–2.0 V vs.  $\text{Li/Li}^+$ ; current density:  $175 \text{ mA g}^{-1}$  (0.5 C); (—) PAA 10wt. %; (---) PVdF 10 wt. %.

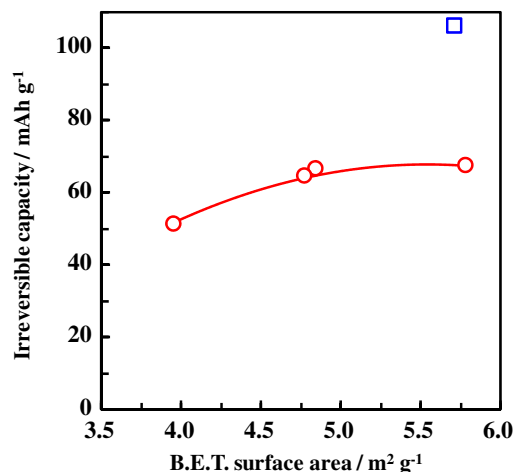
between the  $\text{LiCoO}_2$  particles and graphite particles increased because both the  $\text{LiCoO}_2$  and graphite powders were effectively dispersed by employing ammonium polyacrylic acid (PAA– $\text{NH}_4$ ) as a dispersant, resulting in the improved charge–discharge characteristics of the  $\text{LiCoO}_2$  electrode [4].

Based on these reports, we have focused on a water-soluble polymer of polyacrylic acid (PAA) as the binder and covering agent. Our group has reported that the graphite particle coated with PAA enabled the reversible charge ( $\text{Li}^+$  ion intercalation) and discharge (deintercalation) reaction in a propylene carbonate (PC)-based electrolyte; it could effectively improve the charge–discharge characteristics in an EC-based electrolyte [5]. The PAA as a binder for the natural graphite negative electrode [6], for the Si alloy negative electrode [7], and  $\text{LiFePO}_4$  positive electrode [8] was then reported for use in a lithium-ion battery. However, the detailed mechanism, which PAA exerts on the improvement of the charge–discharge characteristics, has not yet been clarified.

In this study, we focused on the coating state of the graphite particles coated with PAA, the surface deposit of the NG-3 electrode, and the solid electrolyte interface (SEI) formation reaction during the initial charging because it was considered that they



**Fig. 2.** B.E.T. specific surface area of NG-3 electrodes using the prescribed amount of PVdF and PAA as the binders before charging; (○) PAA 10 wt. %; (□) PVdF 10 wt. %.



**Fig. 3.** Relationship between the B.E.T. specific surface area of NG-3 electrodes and the irreversible capacity of 1st cycle; (○) PAA 10 wt. %; (□) PVdF 10 wt. %. Solid curve indicates trend in the experimental data.

would have an influence on the initial charge–discharge characteristics. Considering the further design of a novel binder, we analyzed of the SEI formation reaction and the chemical composition of the surface deposit to obtain primary knowledge about the natural graphite electrode coated with PAA. We have discussed the influence of the difference in the binder types on the SEI formation reaction and the chemical composition of the surface deposit by mainly analyzing the change in the natural graphite electrode surface during the initial charge–discharge cycling.

## 2. Experimental

The graphite electrode was prepared in a way similar to that previously reported [9]. Natural graphite powder (Kansai Coke and Chemical Co., NG-3) as the active material, PAA (Wako Pure Chemical Industries, Ltd.; average molecular weight, 1,000,000) as the binder, and poly(vinylidene fluoride) (Kureha. Co., KF polymer #9130, PVdF) for comparison were employed. A suspension composed of 90 wt. % NG-3 powder and 10 wt. % binder was prepared using a dispersing medium and was then stirred in a reagent bottle at room temperature for 24 h. The percentages by mass of the electrode material in the suspension for the PAA-NG-3 suspension (primarily distilled water as the dispersing medium) and the PVdF-NG-3 suspension (*N*-methyl-2-pyrrolidone (Kanto Chemical Co., 99.0%, NMP) as the dispersing medium) were 20.0 wt. % and 43.5 wt. %, respectively. The suspension was coated on a Ni mesh (Tokyo Screen Co., 100 mesh, 10 mm × 10 mm). The electrode was then pressed for 10 min after air-drying at 80 °C for 1 h. Prior to their use, the PAA-NG-3 electrode and the PVdF-NG-3 electrode were dried in a vacuum at 200 °C and 180 °C for 3 h, respectively.

A three-electrode cell, which consisted of the NG-3 electrode (W.E.), a pressed lithium metal foil on the Ni mesh (R.E. and C.E.), and a  $1 \text{ mol dm}^{-3}$  (M) solution of  $\text{LiClO}_4$  in EC:DEC (diethyl carbonate) (50:50 vol. %) (Mitsubishi Chemical Co.; water content under 10 ppm) as the electrolyte, was employed for the electrochemical measurements. The cells were assembled in a glove box (Miwa Mtg Co., Ltd., DBO-1NKP-1U-2) filled with dry argon at 25 °C. The charge–discharge cycle tests were performed using an automatic battery charging–discharging instrument (Hokuto Denko, HJR1010mSM8) at the current density of  $175 \text{ mA g}^{-1}$  ( $1C = 350 \text{ mA g}^{-1}$ ) between 5 mV and 2.0 V at 25 °C. The AC impedance apparatus consisted of a computer-controlled electrochemical measuring system (Hokuto Denko HZ-5000) and

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