Applied Surface Science 257 (2011) 9110–9119

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

XPS, XRD and SEM characterization of a thin ceria layer deposited onto graphite electrode for application in lithium-ion batteries

Jolanta Świątowska[a,*], Virginie Lair[b], Catarina Pereira-Nabais[a], Gérard Cote[b], Philippe Marcus[a], Alexandre Chagnes[b,*]

[a] Laboratoire de Physico-Chimie des Surfaces, CNRS (UMR 7045), Ecole Nationale Supérieure de Chimie de Paris (Chimie ParisTech), 11 Rue Pierre et Marie Curie, 75005 Paris, France
[b] Laboratoire d'Electrochimie, Chimie des Interfaces et Modélisation pour l'Energie, CNRS (UMR 7575), Ecole Nationale Supérieure de Chimie de Paris (Chimie ParisTech), 11 Rue Pierre et Marie Curie, 75005 Paris, France

ARTICLE INFO

Article history:
Received 1 December 2010
Received in revised form 23 May 2011
Accepted 24 May 2011
Available online 1 June 2011

Keywords:
Lithium ion battery
Ceria
Graphite
SEI layer
Electro-precipitation
XPS

ABSTRACT

Thin ceria layer deposited by electro-precipitation onto graphite was synthesised and characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The electro-precipitated ceria has a cubic structure with nanocrystallites of about 6 nm. The SEM analyses shows that the ceria layer reflects the morphology of the graphite electrode, exhibits small cracks usually found on the electro-precipitated films but covers almost completely the surface of the graphite. The ceria layer is composed of 75% Ce(IV) and 25% Ce(III) oxides as indicated by the XPS analyses. Cyclic voltammetry and galvanostatic charge–discharge tests in ethylene carbonate/dimethyl carbonate (1/1) (wt/wt) in the presence of 1 M $LiPF_6$ show that reversible lithium insertion and deinsertion occurs in the graphite/ceria electrode and that the ceria layer on the graphite electrode prevents from the loss of capacity during the first four cycles. The reduction of the electrolyte occurs at about 0.7 V *vs* Li/Li^+ on both electrodes but XPS and SEM analyses show that the SEI layer is thin and not as homogenous on the graphite as on the graphite/ceria electrode. The composition of the SEI layer on the graphite/ceria electrode, mainly composed of Li_2CO_3, $ROCO_2Li$, $R–CH_2OLi$ and LiF, is different than those obtained on the graphite.

1. Introduction

Efficient lithium-ion batteries must exhibit high charge capacity, high rate capability and also long cycle life. It is generally believed that one of the most important prerequisites for good cycling stability of Li-ion batteries is the formation of a complete and stable passivating layer, called also solid electrolyte interphase (SEI) layer [1] at the negative electrode during the initial charge–discharge cycles. In case of a graphite electrode, a good passivating layer avoids an exfoliation of the graphite by removing the solvation shell around lithium ions. The quality of the passivating layer formed on the graphite electrode depends on the electrolyte composition. Nowadays, ethylene carbonate (EC) is commonly used as a co-solvent in electrolytes for lithium-ion batteries because its reduction leads to the formation of a good passivating layer. Nevertheless, during the charge–discharge cycles, the ageing of this passivating layer induces a drop of charge capacity.

In order to improve the quality of the SEI layer and the electrochemical performances of the Li-ion batteries, numerous studies reported in the literature are related to the development of new electrolytes. For instance, Chagnes et al. studied the influence of various electrolytes on the quality of the SEI and the cycling ability at graphite electrodes [2–6].

Recently, some studies have shown an improvement of the electrochemical performances of the graphite electrodes after modification of the surface structure by mild oxidation [7,8], deposition of metals oxides [9–11], polymer coatings [12,13] and coating with other kinds of carbons [14]. In fact, metal or metal oxide deposition onto graphite electrodes improves the reversible capacity by limiting the exposure of the active edge sites to the electrolyte [15]. For instance, metal oxides containing Sn, Cu, Ni, Fe or Pb deposited on the surface of graphite display higher reversible capacity, better rate capability and longer cycle life in comparison with bulk metal oxides [16–18].

Another approach for improving the electrical performances of negative material for lithium-ion batteries could be a deposition of a "synthetic" passivating layer on the graphite electrode by electro-precipitation. This "synthetic" passivating layer should have a good adhesion to the graphite, allow for a reversible intercalation and deintercalation of lithium and prevent a co-intercalation of solvent

* Corresponding authors.
E-mail addresses: jolanta-swiatowska@chimie-paristech.fr (J. Świątowska), alexandre-chagnes@ens.chimie-paristech.fr (A. Chagnes).

0169-4332/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2011.05.108

molecules into graphite. Ceria (CeO_2) seems to be a good candidate due to its insulating properties that should prevent the reduction of the electrolyte responsible for irreversible capacity fading. Several authors have proposed a modification of the graphite surface with ceria by the immersion of a graphite electrode in a cerium (IV) sulfate solution [19–23], which leads to:

- the formation of a dense oxide layer onto the graphite surface
- the increase of the number of nanochannels, micropores
- the inhibition of the movement of the graphene sheets along *a*-axis
- the decrease of the imperfection of the graphite such as sp3-hydridized carbon atoms, carbon chains and carbon radicals

It was demonstrated that the deposition of ceria layer on the graphite by this method improves the stability and the electrochemical performances of the graphite electrode [24].

Electro-precipitation is another method that can be applied for the deposition of thin ceria layer on the electrode surface. To best of our knowledge, no work concerns the investigation of the physicochemical and electrochemical properties of negative graphite electrodes modified by electro-precipitation for lithium-ion batteries.

In this paper, a thin ceria layer was deposited onto graphite by electro-precipitation and the physicochemical properties of this material were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) before and after lithium insertion/deinsertion in a solution of lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate/dimethyl carbonate (1/1) (wt/wt). The electrochemical properties (the reversible and the irreversible capacities) of the graphite/ceria electrode were investigated by cyclic voltammetry and galvanostatic charge–discharge and compared to graphite electrode.

2. Experimental

2.1. Electrochemical experiments

Electro-precipitation of ceria was performed in a three-electrodes electrochemical cell by using graphite (0.7–0.8 cm^2) provided by SAFT Company (France), a platinum grid and an Ag/AgCl electrode ($E_{Ag/AgCl}$ = 0.2 V *vs* NEH) as working electrode, counter electrode and reference electrode, respectively. The electro-precipitation of ceria was performed with a rotating disc electrode at 300 rpm.

The electro-precipitation of ceria onto graphite was performed at room temperature (20 ± 2 °C) in 0.1 mol L^{-1} $NaNO_3$ and 0.1 mol L^{-1} $Ce(NO_3)_3$ solution prepared with ultra pure Millipore® water (resistivity >18 MΩ cm) and reagent grade chemicals (Aldrich). The electrochemical cell was bubbled with pure dioxygen (Alpha Gaz 1, 99.995%, Air Liquide) during 30 min before and during the electro-precipitation of ceria. The electro-precipitation was performed by applying a constant potential of −0.8 V *vs* Ag/AgCl for 90 min using an EG&G PAR model 263A potentiostat [25,26]. After the electro-precipitation, the graphite/ceria sample was rinsed with ultra pure water and dried in an argon flow at room temperature.

The study of the insertion/deinsertion of lithium ions into the graphite/ceria electrode was performed by cyclic voltammetry with an Autolab (AUT30) potentiostat/galvanostat in a glove-box directly connected to the ultra-high vacuum XPS analysis chamber [27].

The electrochemical tests were carried out in Swagelok half-cells (graphite electrode/Li or graphite/ceria electrode/Li) containing a polypropylene separator (Celgard® 2000) to separate the anodic and cathodic compartments. The cyclic voltammetry of the graphite/ceria electrode was performed at 0.1 mV s^{-1} from the open circuit potential (3.2 V *vs* Li/Li^+) to 0.005 V *vs* Li/Li^+ at room temperature in a solution of 1 M $LiPF_6$ (purity > 99.99%, battery grade, Aldrich) in ethylene carbonate (EC, purity = 99%, Aldrich) and dimethyl carbonate (DMC, purity = 99%, Aldrich) [EC/DMC (1/1) (wt/wt)]. The cyclic voltammetry of the graphite electrode was performed between 1.4 and 0.005 V *vs* Li/Li^+.

The galvanostatic charge–discharge tests of half and full-cells of the graphite/ceria and graphite electrode were operated at *C*/20 charge and discharge during 20 h in the same electrolyte. Half-cells were charged at constant current to a cut-off voltage of 0.01 V *vs* Li^+/Li. Discharge was operated at constant current, to a cut-off voltage of 3 V *vs* Li^+/Li.

2.2. X-ray diffraction (XRD)

X ray diffractograms were recorded with an X'Pert Pro apparatus from PANalytical using Cu Kα radiation (λ = 1.5406 Å), equipped with an incident beam Ge (1 1 1) monochromator and a linear Pix-Cell detector (active length 14 mm). XRD data were recorded in a scanning mode between 15° and 0° at every 0.026° 2θ. X-ray generator worked at 45 kV and 40 mA. All the data were processed by X'Pert HighScore software with his commercial databases (background deduction, profile fitting, and peaks identification).

2.3. X-ray photoelectron spectroscopy (XPS)

XPS analyses were carried out with a VG ESCALAB 250 spectrometer equipped with a UHV preparation chamber directly connected to the glove box [27]. Base pressure during analysis was $\sim 1 \times 10^{-9}$ mbar. An Al Kα monochromatized radiation ($h\nu$ = 1486.6 eV) was employed as X-ray source. For all analyses, the take-off angle of the photoelectrons was 90°. High resolution spectra of the Ce 3d, O 1s, C 1s, N 1s and Li 1s core level regions were recorded with a pass energy of 20 eV. The data processing (peak fitting) was performed with the Avantage software provided by Thermo Electron Corporation, using a Shirley type background subtraction and Gaussian/Lorentzian peak shapes. The binding energies were corrected by setting the C 1s hydrocarbon (–CH_2–CH_2–bonds) peak at 285.0 eV for the graphite electrodes and the uIII line at 917.0 eV for the graphite/ceria samples. The XP spectra were recorded on the pristine graphite, graphite/ceria samples and after two cycles of lithium insertion/deinsertion in a deinserted state.

2.4. Scanning electron microscopy (SEM)

SEM pictures were obtained from a scanning electronic microscope LEO DSM 892 Gemini equipped with energy-dispersive X-ray (EDX) analyzer. The samples were washed with dry DMC and the remaining solvent was evaporated at room temperature.

3. Results and discussion

3.1. Mechanisms of electro-precipitation of ceria

During the electro-precipitation of ceria onto graphite at −0.8 V *vs* Ag/AgCl in an aqueous solution of $NaNO_3$ and $Ce(NO_3)_3$, the following electrochemical reactions occur in addition to the electro-precipitation of ceria:

$$O_2 + 2H_2O + 4e^- = 4OH^-, \quad E^\circ = 0.40\,V/NHE \tag{1}$$

$$H_2O + e^- = 1/2H_2 + OH^-, \quad E^\circ = -0.83\,V/NHE \tag{2}$$