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Electrochemical behavior of pure graphite studied with a powder microelectrode

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ABSTRACT

In this work, cyclic voltammetry and electrochemical impedance spectroscopy (EIS) techniques have been used to study the lithiation/delithiation of graphite using powder microelectrode in a 1.2 M $LiPF_6$ in EC:EMC electrolyte. The advantage of using the powder microelectrode is the possibility to easily study graphite without any additive and determine electrochemical characteristics of Li-insertion. The use of cyclic voltammetry at very low scan rates allows to estimate the diffusion coefficient of lithium inside graphite. The exchange current density of graphite for several state of charge (SoC) has also been determined by EIS measurements. Moreover, the powder microelectrode is a useful tool to study the formation of the solid electrolyte interphase (SEI) on graphite either by cyclic voltammetry or EIS.

1. Introduction

Due to its low cost and relatively high gravimetric capacity (372 mAh g^{-1}), graphite has been widely studied for lithium-ion battery applications as an efficient candidate for negative electrode material [1]. The intercalation of lithium inside the graphite is a reversible process occurring at low potentials *vs* Li, and a detailed investigation of the kinetics of this process remains challenging. Indeed, electrodes in battery systems usually consist in a composite porous electrode, that is for the negative electrode, a mixture of electroactive graphite, conductive carbon and of a polymer binder. As a result, the electrochemical response of the composite electrode is no longer the electrochemical response of the active material itself, thus requiring to develop techniques for studying the active material separately. Interestingly, several techniques have been devised for studying the active material only (*i.e.* without any additive), and most of them required the use of microelectrode-based techniques [2–4]. Indeed, it consists in contacting a single particle of material with a current collector and to perform electrochemical measurements on the selected grain. With such a technique, Nishizawa et al. [5,6] reported on the electrochemical response of a mesocarbon single particle pressed against a Ni band microelectrode. The study of Li insertion inside graphitized carbon [7] and disordered carbon [8] by means of electrochemical impedance spectroscopy (EIS) has also been performed. Similarly, Positive electrode materials have been studied such as $LiMn_2O_4$ [9–12] or $LiCoO_2$ [9,10,13,14]. In particular, kinetic characterizations of $LiMn_2O_4$ [11] and $LiCoO_2$ [14] particles have been realized where the diffusion coefficient of lithium inside the material have been estimated by Potential Steps methods and EIS.

Another approach for studying pure battery materials is the powder microelectrode also called the cavity microelectrode [15–21]. This technique consists in inserting a small amount of material (still without any additive) inside a micrometer-sized cavity to perform electrochemistry on few grains. Interestingly, compared to the single particle technique, it does not require to work under a microscope for connecting the grain to the current collector, and hundreds of cycles can be readily performed as illustrated on polyaniline [17] and hydride materials [22]. Li-insertion battery materials powders such as V_2O_5 [21], $LiMn_2O_4$ [16], a mixture of $LiMn_2O_4$ with graphite [20] or a mixture of $LiFePO_4$ with conductive carbon [19] have been successfully studied electrochemically (CVs) using a cavity microelectrode.

The aim of this work is to show that it is possible to use a cavity microelectrode for studying Li insertion in graphite powder without the adjunction of conductive carbon or any binder, which has never been realized before. Our choice was directed towards the cavity microelectrode technique rather than the single particle measurement for several reasons. Performing electrochemical tests on a single particle requires specific equipment, the contact between the particle and the microelectrode is tedious because of the swelling of the material upon lithiation, and a current in the pA range or less for performing efficient

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charge/discharge cycles is very small. With a cavity microelectrode, no special equipment is required, the contact would not depend on the swelling and the currents are sufficiently high (in the nA range or larger) for cycling the material. In this work, the insertion/deinsertion of lithium inside the graphite particles is investigated by cyclic voltammetry and EIS at different insertion ratio.

2. Experimental

The insertion/deinsertion reactions of Li in graphite were investigated using a home-made cavity microelectrode [17,18]. Most of the results presented in the literature consisted in using a Pt microwire sealed by heating in a borosilicate glass capillary. The extremity of the wire was then dissolved in order to form a microcavity, in which the material was inserted. For studying graphite, platinum is not a good candidate as current collector since it alloys with Lithium. It was thus advantageously replaced by a copper microwire (150 µm in diameter), which was inserted inside a capillary glass and sealed at the bottom with an epoxy resin. The microelectrode was then polished using sandpaper (P4000), exposing a copper microdisk at the apex of the electrode. In a last step, the cavity was obtained by anodic dissolution of copper in a 1 M KCl solution. The depth of the cavity was controlled with the duration of the dissolution and checked with optical observations. The cavity is then filled by pressing the electrode against graphite powder (Fig. 1a). All electrochemical measurements were performed in a three-electrode configuration (Fig. 1b) using a cavity microelectrode as working electrode and two Li metal strips as counter and reference electrode, respectively.

The graphite powder was provided by POSCO. Its active surface area was about 3 m^2/g and the average particle size obtained from SEM observations was 15 µm in diameter (*vide infra*). The electrolyte consisted in a 1.2 M $LiPF_6$ in an EC:EMC (3:7 vol.) mixture. The cell was assembled in an argon-filled glovebox (oxygen and water content below 1 ppm). All the electrochemical experiments were performed in the glovebox using a GAMRY REF 600+ potentiostat. Before each experiment, cavity was cleaned by sonication in a water/ethanol mixture (1:1 vol.) for 15 min.

3. Results and discussions

3.1. Cyclic voltammetry experiments

The electrochemical kinetics of lithiation/delithiation processes of graphite was first studied by cyclic voltammetry starting from 1 V/Li/Li^+ at several scan rates (Fig. 1c). During the reduction scans, a small shoulder followed by a plateau is observed at *ca.* 0.6 V/Li/Li^+. This irreversible process is ascribed to the formation of a passivating layer, the solid electrolyte interphase (SEI), around the particles and is observed for the first cycles, only. At lower potentials, the staging for lithium insertion at different potentials between 0.2 and 0 V/Li/Li^+ corresponding to peaks more or less well-defined, can be identified. When the scan rate increases from 20 to 200 µV/s, the contribution to the SEI formation gradually decreases with the cycle number, and we clearly see a polarization phenomenon, which reflects the electrochemical response by both an enlargement and an overlapping of the insertion peaks. Similarly, on the oxidation domain, the delithiation of graphite particles resulted in a multi-steps processes, with an increase of the overpotential with the scan rate.

When the cyclic voltammetry was performed at 20 µV/s (blue curve in Fig. 1c), two insertion peaks are well defined. However, for potential lower than 50 mV/Li/Li^+, a strong increase of the reduction current is observed, and a fine analysis of the electrochemical signal is no longer possible.

By decreasing the scan rate to 5 µV/s (Fig. 2a), we approach the steady-state behavior, allowing a better visualization of all the individual stages for lithium insertion inside the graphite flakes. During

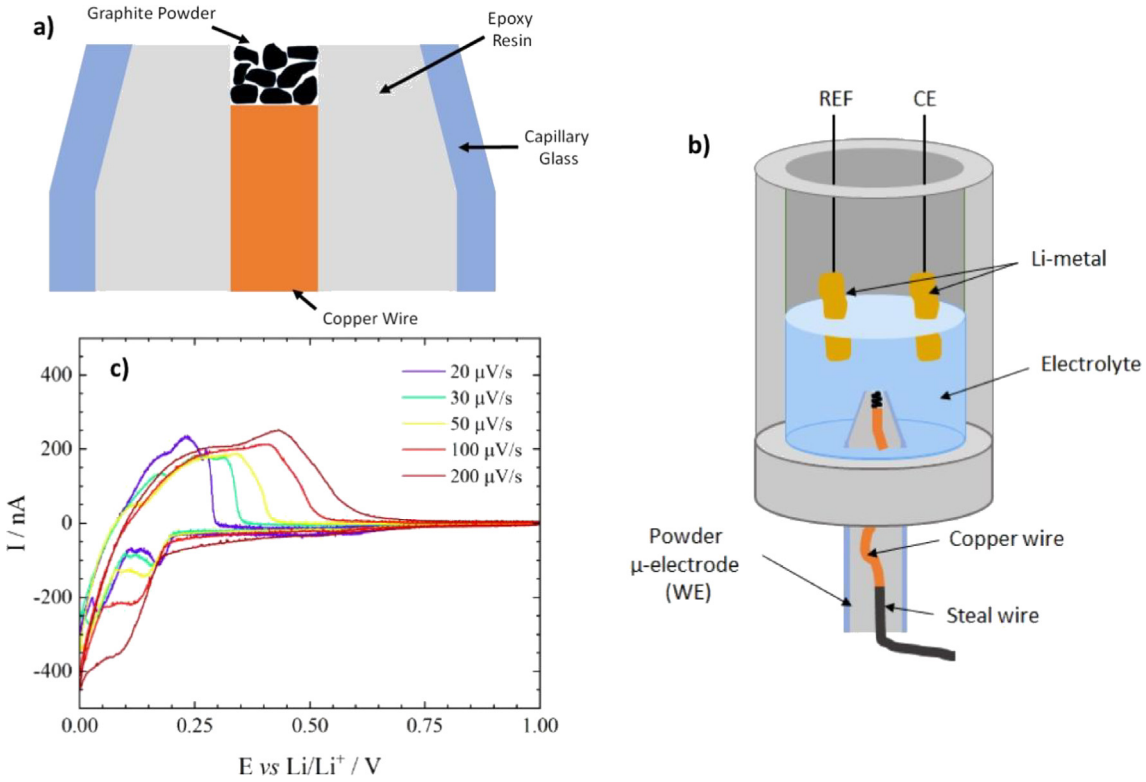

Fig. 1. (a) Schematic representation of the powder microelectrode; (b) Experimental set-up where the powder microelectrode is immersed in a 1.2 M $LiPF_6$ EC:EMC (3:7 vol.) electrolyte trapped in a Teflon cell; (c) Cyclic voltammetry performed on the powder microelectrode as a function of the scan rate. (For interpretation of the references to color in this figure, the reader is referred to the online version of this chapter.)