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Impact of the metal electrode size in half-cells studies: Example of graphite/ Li coin cells



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Keywords: Li metal electrode size Graphite electrode Electrochemical performance Interphase formation XPS	When half-cells are used to evaluate and understand electrochemical performance and interface properties of a given electrode, the metal electrode size is rarely mentioned. To evaluate such impact on the electrochemical performance and interphase formation, graphite/Li coin cells were used. Undersizing the Li metal electrode led to significantly lower charge/discharge capacities even at C/20 rate due to incomplete lithiation/delithiation processes of the graphite electrode edge. It also led to the formation of non-uniform Li metal deposits as well as to a graphite SEI film with a thickness and composition gradient across the electrode. Oversized Li led, however to homogeneous graphite SEI film. Overall, these results highlight the critical role of the metal electrode size in half-cells and should apply to all half-cells studies using other metal electrodes such as Na, K, Mg.

1. Introduction

Since the introduction of the solid electrolyte interphase (SEI) [1] model to describe the surface films that forms at the electrode/electrolyte interfaces by degradation of electrolyte solvents and/or salts under cycling/storage of Li-ion cells, numerous studies have been reported [2-5]. Most of these studies use, however, half-cells with Li metal as the counter electrode, which is unlikely to depict full-cells for various aspects. First, the Li metal is likely to act as an infinite source of Li. Second, the high reactivity of the lithium metal against the electrolyte is likely to produce more and/or different electrolyte degradation species that have a high probability to migrate to the studied electrode surface then interact. Such phenomenon is called interactions between electrodes or cross-talk [6-8] the most known being the dissolution of positive active materials at high voltage and the deposition of metal-based species at the negative electrodes surface [9]. This topic still suffers, however, a lack of attention despite recent dedicated studies [10–15]. As a whole, in half-cells, the use of a theoretical infinite source of Li and the interactions between electrodes can greatly alter the electrochemical performance and the interphase of the studied electrode. Therefore, the half-cells should be preferably restricted to electrochemical mechanism studies of new material rather than used to extrapolate and predict the full-cells behaviour. Moreover, despite the plethora of half-cells studies, the Li metal electrode size (i.e. the surface area) is almost never mentioned probably because it is considered as an infinite source of Li. This means that, the Li metal electrode surface area

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Here, as the Li metal surface area may be crucial to both the electrochemical performance and interphase formation, this impact was investigated in the case of graphite/Li cells.

2. Experimental

2.1. Cell preparation and cycling protocol

The electrolyte was 1 M LiPF₆ (battery grade, purity \geq 99.99%) in EC (anhydrous, 99% purity):EMC (purity \geq 98%) with a 3:7 weight ratio (water content < 50 ppm), from Aldrich. Graphite electrode, made of artificial graphite:CMC + SBR:carbon black with a 95.7:2.9:1.4 weight ratio (6.15 $mg_{graphite}/cm^2,~60~\pm~2\,\mu m$ thick after calendaring), coated on a copper foil (9 μm thick), were obtained from S4R (Castelnau-le-Lez, France). Graphite electrodes were heated at 80 °C under vacuum for 12 h. Graphite/Li 2032 coin cells were assembled under Ar with 0.11 ml of electrolyte and two PPP separators. Note that varying the electrolyte amount is more likely an important parameter when studying the interphase formation but have been kept constant and in excess (due to the coin cell mounting) in the present case. The graphite/Li surface area ratio was set to $0.95 \text{ cm}^2/1.13 \text{ cm}^2 = 0.84 (Gr/$ Li-0.8 cells) and $1.27 \text{ cm}^2/0.64 \text{ cm}^2 = 1.98$ (Gr/Li-2 cells). The latter (i.e. 1.98 ratio) was selected so that if significant changes have occurred, they could have been observed visually and they could have

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Fig. 1. a) Potential versus time curves and b) charge capacity $(mA.h/g_{graphite})$ versus the specific current J $(mA/mg/cm^2)$ for the Gr/Li-2 and Gr/Li-0.8 cells. The notation "bis" stands for the second pair cell.



Fig. 2. Photographs of the lithium and graphite electrodes as extracted from the a) Gr/Li-0.8 and b) Gr/Li-2 cells with respect to the real scale. Red spots indicate area where XPS analysis was performed. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

been characterized by XPS at different positions along the oversized graphite region considering an elliptic X-ray beam spot of about $450 \times 900 \,\mu\text{m}$.

Using a MPG battery cycler (Biologic SA, France), cells were held at OCV during 30 min for wetting completion then cycled between 0.005 and 1.2 V at C/20 for two cycles. Cells were discharged to 0.005 V at C/20 followed by a potential hold at 0.005 V until a C/100 current was reached. A power test was performed by successive charge current pulses of C/3, C/5, C/8, C/10, C/15, C/20 with a 1 h OCV relaxation between each pulse. A final cycle was performed between 0.005 and 1.2 V at C/20. All currents refer to $372 \text{ mAh/g}_{\text{graphite}}$, i.e. all currents were set according to the individual graphite electrode mass so that a given current in mAh/cm² was strictly identical whatever the electrode was.

Coin cells were then opened under argon and graphite electrodes were washed twice by immersion in a glass vial containing 0.8 ml of EMC during 10 s.

2.2. X-ray photoelectron spectroscopy (XPS)

XPS was performed using an Escalab 250 Xi spectrometer using a monochromatized Al K α radiation (h ν = 1486.6 eV). Electrode samples were put on a sample holder using an insulating uPVC tape (reference 655 from 3 M) then the samples transfer was performed through an

argon-filled glove box directly connected to the spectrometer. Before analysis, samples were kept at 10^{-8} mbar for one night. Analysis was performed using the standard charge compensation mode and an elliptic 450 × 900 µm X-ray beam spot. Core spectra were recorded using a 20 eV constant pass energy with a 0.15 eV step size and short time iterative scans. Using CasaXPS software, the binding energy scale was calibrated from the 285 eV peak (C–C/C–H). A non-linear Shirley-type background was used for core peaks analysis while 70% Gaussian - 30% Lorentzian Voigt peak shapes and full width at half-maximum constraint ranges were selected to optimize areas and peak positions. XPS quantification was performed using the relative sensitivity factor provided with the Escalab machine.

3. Results

3.1. Electrochemical performance

Fig. 1 shows a) the potential versus time curves and b) the charge capacity versus the specific current J (mA/mg/cm²) for Gr/Li-0.8 and Gr/Li-2 cells. Both cells showed very close shape of the discharge/charge curves with the reversible lithiation stages of the graphite [16]. Gr/Li-2 cells showed, however, shorter discharge/charge time compared to Gr/Li-0.8 cells (Fig. 1a) due to lower capacities (Fig. 1b). Indeed, Gr/Li-2 cells delivered about 5.5% lower charge capacity

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