



Li distribution in graphite anodes: A Kelvin Probe Force Microscopy approach



Sergey Yu. Luchkin^{a,*}, Hugues-Yanis Amanieu^b, Daniele Rosato^b, Andrei L. Kholkin^{a,c}

^a Dept. of Materials and Ceramic Engineering & CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

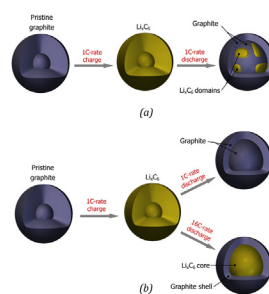
^b Advanced Functional and Sintered Materials-Material Characterization and Component Design (CR/ARM1), Robert Bosch GmbH, Postfach 10 60 50, 70049 Stuttgart, Germany

^c Ural Federal University, Lenin Ave. 51, Ekaterinburg 620083, Russia

HIGHLIGHTS

- We observed a core–shell surface potential on graphite particles of an aged anode.
- We observed a mosaic surface potential on graphite particles of an unaged anode.
- Our results corroborate “radial” and “mosaic” models of Li distribution.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 30 April 2014

Received in revised form

17 June 2014

Accepted 25 June 2014

Available online 7 July 2014

Keywords:

Li battery

Anode

Graphite

C rate

KPFM

ABSTRACT

Advanced Li-ion batteries with high energy and power densities are urgently required in many applications including automobiles. Aging of these batteries and irreversible capacity loss are still the factors preventing their further use, and novel methods of their study are prerequisite for the understanding of degradation at nanoscale. In this work, we use Kelvin Probe Force Microscopy (KPFM) to assess the distribution of surface potential in graphite anodes of commercial Li-batteries before and after aging at high C rates. In the aged sample, we observed an apparent core-shell-type potential distribution on large crack-free particles. We attribute this core-shell potential distribution to the remnant Li^+ ions stacked in graphite particles causing irreversible capacity loss. The results corroborate the “radial” model used to explain the specific capacity fading mechanism at high C rate cycling in commercial batteries.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Growth in popularity of electric vehicles and green technologies requires safe, long lasting, and high performance batteries. Conventional Li-ion batteries are only efficient for low-current applications such as mobile devices, but do not satisfy the needs of

emerging high-power automotive and renewable energy applications. Higher cycling rate (C rate) in these devices causes faster degradation and lower specific capacity after prolonged use [1]. The improvement and optimization of Li-ion batteries require a complex study of the implemented electrode materials (cathode, anode and electrolyte) all involved in Li transfer. It is prerequisite to study the Li transport and diffusion at the highest resolution possible for deeper understanding of the aging processes taking place in battery materials during intensive cycling.

* Corresponding author.

E-mail addresses: luchkin@ua.pt, useluch@gmail.com (S.Yu. Luchkin).

Scanning Probe Microscopy (SPM) based techniques such as Electrochemical Strain Microscopy (ESM) [2] and Kelvin Probe Force Microscopy (KPFM) [3] were therefore used to study aging mechanisms at the meso- and nanoscales (i.e. within the grains of active materials). Recently, Nagpure et al. have implemented KPFM to measure the surface potential (SP) of aged and unaged LiFePO_4 cathodes [4]. They found that the surface potential of aged samples is lower than of the unaged ones. In another work, Jing Zhu et al. [5] used KPFM to study the change of surface potential of the TiO_2 anode in an all-solid-state Li-ion battery during Li insertion and extraction. These works clearly demonstrated a great potential of KPFM for the characterization of battery materials at the mesoscale. However, stronger experimental evidence is required in order to implement KPFM quantitatively with respect to Li concentration in host material.

In this work, we used KPFM to study aging phenomena of the commercial 18650 Li-ion batteries with a graphite anode and a typical capacity of 1200 mAh. We measured surface potential in fresh and aged (<80% State of Health (SOH), discharged at 16C-rate) graphite anodes: one from a discharged cell and the other one from a half charged cell. We observed a clear core–shell surface potential distribution within big dense particles of the aged sample in contrast to the fresh sample. Such structure is attested to remnant Li^+ ions stacked in the core region of the particles. The obtained results are used to explain the specific capacity fading at high C rates caused by degradation within the active grains.

2. Methodology

First, a Li-ion battery cell (“fresh” further in the text) was completely discharged at 1C-rate in CC/CV mode down to 2.3 V with a stop current of 0.2C-rate. A second Li-ion battery cell (termed “aged” further in the text) was cycled being charged at 2 A (slightly more than 1C-rate) and discharged at 16C-rate (Fig. 1). After aging down to 80% SOH, it was finally discharged at 1C-rate. A third Li-ion battery cell (called “lithiated” further in the text) was cycled as the second one down to 78% SOH, then cycled two times at 1C-rate, and charged to 50% State of Charge (SOC) at 1C-rate.

The batteries were opened in an argon filled glovebox; graphite anodes were extracted, carefully washed in dimethyl carbonate (DMC), and embedded in a soft and compliant epoxy resin. After hardening the samples were sequentially polished with 1200–4000 silicon carbide sand paper, 3 μm and 1 μm diamond

paste, and Struers OP-S suspension. Final ion polishing was made by an Ar ion beam: 15 min cleaning at a 10° angle and 30 min polishing at a 4° angle. RMS roughness measured on cross-sections of graphite particles was 11.1 ± 0.4 nm.

Surface potential of the samples was measured by means of a 2-pass amplitude modulated Kelvin Probe Force Microscopy (AM-KPFM) [6] implemented in the NT-MDT Solver Next commercial SPM. In this technique, surface potential is generally a measure of the work function difference between the tip and the sample:

$$V_{\text{CPD}} = \frac{W_{\text{tip}} - W_{\text{sample}}}{e} \quad (1)$$

Here W_{tip} is the work function of the SPM tip, W_{sample} is the work function of the sample, e is the elementary charge, V_{CPD} is the measured contact potential difference, viz. surface potential. During the first pass, the cantilever measures the surface topography, during the second pass the lifted cantilever follows the surface topography at a given height and measures the surface potential via a null method. AC voltage of the second pass was 0.5 V in amplitude, lifting height was always 15 nm; scan resolution is 256×256 points.

It is known that AM-KPFM has lower special resolution than FM-KPFM [7,8]. However, AM-KPFM has higher sensitivity to contact potential difference (energy resolution) and can detect lower minimum detectable ΔV_{CPD} as compared to FM-KPFM [6,8]. Higher sensitivity is important for the detection of smallest changes in surface potential caused by gradual change of Li concentration in graphite. To avoid the shift of SP measured on a biased device in AM-KPFM mode, [7] the investigated samples were not biased.

We used Pt/Ir coated cantilever (NTMDT NSG10, resonance frequency = 249.4 kHz, force constant = 11.8 N m^{-1}) that was calibrated on sputtered Au thin film. Calibration and measurements were performed in ambient conditions at relative humidity (RH) 40%. Measured contact potential difference between the Au film and the tip was $V_{\text{CPD}} = (57.8 \pm 0.3) \text{ mV}$. According to the recommended values of work functions [9] (see Table 1), V_{CPD} should be in the $-(19\text{--}11) \text{ mV}$ range. The difference can be explained by the impact of the ambient humidity, resulting in the absorbed water layer that can screen the work function difference. [10] Note that presented in literature work function values for Au and Pt are scattered in a wider range as compared to those presented in Table 1.

3. Results and discussion

The cycle life of the aged cell shows a clear activation step during the 5 first cycles, i.e. the discharge capacity increases (see Fig. 2). The 20 following cycles show a slow decrease in the capacity. This behavior can be explained by the fact that some lithium ions are not yet activated. Two processes with opposite trends run in parallel. On one hand, more and more lithium ions are involved into an electrochemical process upon cycling, increasing the capacity. On other hand, some lithium ions are being consumed due to ageing phenomena, hence being passivated and decreasing the capacity. After a while the first process becomes insignificant, explaining the

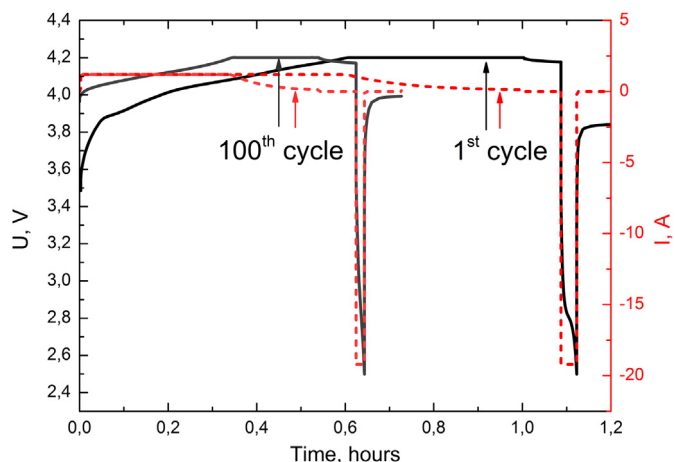


Fig. 1. Charge-discharge curves of the aged to 80% SOH sample for the 1st and the 100th cycles. Battery was charged in the CC/CV mode at 2 A current until voltage reach 4.2 V and then discharged at 16C-rate.

Table 1
Recommended work functions for polycrystalline materials [9].

Material (polycrystalline)	Work function, eV
Au	5.31 ± 0.07
Pt	5.27 ± 0.08
Cu	4.51 ± 0.07
Graphite	$4.6 \pm 0.1; 5.0$

Download English Version:

<https://daneshyari.com/en/article/7736279>

Download Persian Version:

<https://daneshyari.com/article/7736279>

[Daneshyari.com](https://daneshyari.com)