



# The Effect of Pre-Analysis Washing on the Surface Film of Graphite Electrodes



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## ABSTRACT

Electrodes are routinely washed to remove electrolyte deposits, salt, and high boiling point solvents prior to analysis with surface-sensitive techniques. The effect of washing on the surface films of graphite electrodes from LiCoO<sub>2</sub>/graphite cells, which contained varying amounts of vinylene carbonate (VC), was investigated by comparing the microstructure and chemical composition. We confirmed that there are two different kinds of films on the surface of the electrodes: one at low and one at high VC content concentration. Far from being limited to remove extraneous salt deposits from the surface of the sample, DMC washing was found to completely remove one and to affect the composition of deeper strata in the other.

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## 1. Introduction

Lithium-ion cells are the energy storage solution of choice in most handheld and portable electronics. However, the power and capacity of these cells can be reduced considerably dependent on storage and usage conditions [1]. For a mobile phone or a laptop computer, with short innovation cycles where it is replaced by a newer model every couple of years, this is not a significant problem. For cells used in vehicles and medical electronics, which are used for much longer (8+ years), battery degradation issues present considerable challenges in maintaining power and capacity over the cells' lifetimes [2].

A single lithium-ion cell consist of two electrodes separated by a permeable polymer membrane. Ion transport is facilitated between electrodes by the electrolyte. The negative electrode is most often graphite and the positive electrode lithiated metal oxide. The electrolyte usually consists of a mixture of organic carbonates and a lithium salt. Within the first few cycles of a lithium-ion cell, a film is formed at one [3] and perhaps both electrodes [4]. This film, a solid electrolyte interphase (SEI) [5] layer, passivates the electrode surface to further reaction with the components of the electrolyte [6]. The study and characterization

of these films, to determine their chemical composition and properties, have been the subject of many years of research. The knowledge gained from these studies could lead to improvements in cell lifetime or performance.

Before characterizing the surface film, most authors wash the electrode with a low boiling point solvent. Lu et al. report that the reason for this is to remove higher boiling point electrolyte solvents [3]. Yang et al. report that, in addition to removing the electrolyte solvent, washing also removed residual salt which had been deposited onto the electrode after the more volatile electrolyte components had evaporated [4].

There is a distinct possibility that the washing process, which in some cases is quite prolonged [7], may affect the composition of the SEI or partially remove it. Dedryvère et al. used acetonitrile to remove PEO oligomers, Li<sub>2</sub>CO<sub>3</sub> and CH<sub>3</sub>OCO<sub>2</sub>Li from the surface of stainless steel electrodes, allowing them to study the underside of the surface film [8]. Malmgren et al. rinsed electrodes with DMC and found that the sensitivity of the exposed graphite to air increased after the rinsing process [9]. They conclude that the increased sensitivity of electrodes to air shows that the rinsing process has removed the passivating surface film.

In addition, Williard et al. state that washing with solvent may lead to removal of SEI [10]. Whilst Orsini et al. state that washing is always the subject of controversy [11]. If analysis is performed on these washed (hence, possibly chemically changed) SEI films, the conclusions may be incorrect.

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In this paper, we report the effect that washing has on the SEI films of graphite electrodes from LiCoO<sub>2</sub>/graphite cells that also contained small amounts of vinylene carbonate (VC). Vinylene carbonate is well known to have a positive effect on a cell's performance over its lifetime and this performance peaks somewhere between 1 and 2% [12]. The reason for this is due to a reaction at the negative electrode to change the composition of the surface film. VC is used because it helps to elucidate the effect that washing has on the electrodes.

To determine if washing only removes salt and solvent, we characterized the surface film of both washed and unwashed negative graphite electrodes using x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and attenuated total reflectance (ATR) Fourier transform infra-red (FTIR) spectroscopy.

## 2. Experimental

### 2.1. Materials

Aged, 300 mAh LiCoO<sub>2</sub>/graphite pouch cells, containing 0, 1, 2, 4, and 6 vol. % VC, were used in this work. The electrolyte in these cells was 1 M LiPF<sub>6</sub> in ethylene carbonate (EC)/ethyl methyl carbonate (EMC), 3:7, by wt. They were cycled between 3.78 V and 4.2 V nine times over 12 days at a rate of C/10 and under ambient conditions.

The cells were then discharged to 0.5 V and dismantled in an argon-filled glove box. The cathode/separator/anode roll was unwound and samples were cut from the bulk of the electrode material using stainless steel scissors. Care was taken to handle the samples with tweezers by the edges. Half of the electrode samples were washed, placed into small evaporating dishes that contained 1.5 mL of dimethyl carbonate (DMC), and left for 2 minutes. The samples were then removed from the DMC and allowed to dry in the glove box for less than 5 minutes.

The other half of the electrode samples were not washed. These samples were prepared in the same way and placed into evaporating dishes, but without DMC.

### 2.2. Characterization

After unwinding and harvesting the electrodes in a glove box, samples were transferred to an adjoining glove box via a common antechamber for analysis using IR and XPS. During this transfer, samples were exposed to pressures around  $1.0 \times 10^{-4}$  kPa for 15 minutes.

Infra-red spectroscopy was performed using a Perkin Elmer Spectrum 100 Fourier-transform, IR spectrometer in attenuated total reflectance mode, using a diamond crystal. A background

spectrum was collected prior to data collection. The total force applied to the samples was kept constant.

Scanning electron microscope samples were transferred to the microscope using a custom-made, air-tight sample holder, which was adapted from that used by Howe et al. [13]. Micrographs were collected on a JEOL JSM 6610LV scanning electron microscope using an accelerating voltage of 10 kV and a working distance of 15 mm using a secondary electron detector.

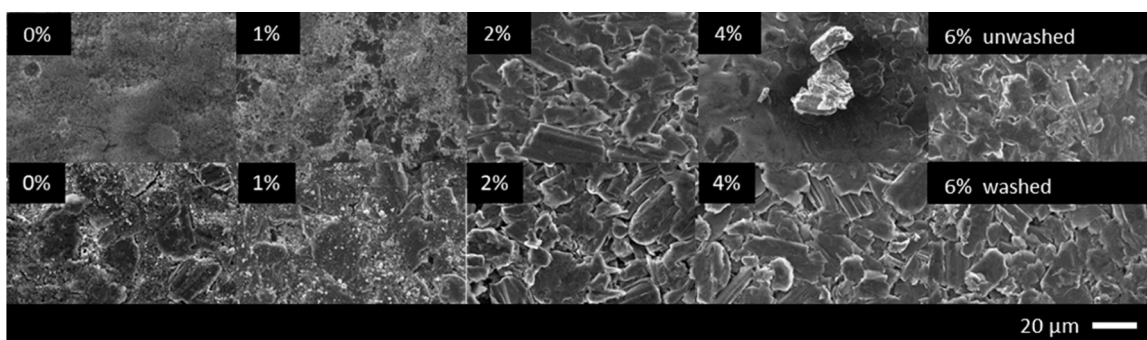
X-ray photoelectron spectroscopy samples (10 × 10 mm) were mounted on a sample holder by means of double-sided tape. Spectroscopy was performed using a Physical Electronics 5000 VersaProbe II with a monochromatic aluminum K $\alpha$  (15 kV) X-ray source. The excitation beam size employed was 100  $\mu$ m and the power was 25 W. Pressures of the system were between  $2 \times 10^{-10}$  kPa before sample insertion and  $2 \times 10^{-9}$  kPa immediately after. Ar<sup>+</sup> ion sputtering was performed at 500 V over an area of 3 × 3 mm. Spectra were recorded in Fixed Analyzer Transmission mode, using a pass energy value of 11.75 eV, step size of 0.1 eV and acquisition time of 2.7 s/step acquisition time. Binding energy correction was carried out assuming that the main component of the C1s region after sputtering corresponds to C-C (graphite) environments at 284.4 eV, and before sputtering was C-C/C-H environments at 284.8 eV.

## 3. Results and Discussion

### 3.1. Morphology

Fig. 1 shows SEM micrographs of the surface of the graphite electrodes harvested from a series of aged LiCoO<sub>2</sub>/graphite cells with varying contents of VC additive (see *Experimental*). The top row corresponds to unwashed electrodes and the bottom row to electrodes washed in DMC prior to examination.

For the unwashed samples, no surface film was apparent on electrode surface for the cell containing 2% VC; two different surface films were visible on the other samples, depending on the concentration of VC. The first of these was visible with 0 and 1% VC. This film was comprised of individual particles that were 1–5  $\mu$ m in length and 2  $\mu$ m in width. Graphite was visible beneath these particles at 1% VC, whereas it wasn't at 0% VC. The particles appeared visually identical in size and structure suggesting that only the quantity of the particles was reduced when 1% of VC was added to the electrolyte. A film with a different structure was visible at the surface of the 4 and 6% VC additive graphite electrodes and it appeared as a solid layer that covered the graphite particles. This covered the grain boundaries in such a way that determining where one particle started and another stopped was not possible. In addition, no constituting particles were observed in the surface film for the 4% and 6% VC content when imaged at the



**Fig. 1.** SEM images of graphite electrodes harvested from LiCoO<sub>2</sub>/graphite cells with varying concentrations of VC in the electrolyte (concentration indicated in labels). The washed electrodes (bottom row) were immersed in DMC and left to dry prior to analysis; the unwashed electrodes (top row) were simply let dry.

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