ARTICLE IN PRESS

Extreme Mechanics Letters ▮ (▮▮▮▮) ▮▮▮–▮▮▮

Contents lists available at ScienceDirect

Extreme Mechanics Letters

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

Internal stress due to solvent co-intercalation in graphite electrodes for Li ion batteries

Brian W. Sheldon *, Anton Tokranov

School of Engineering, Brown University, Providence, RI 02912, United States

ARTICLE INFO

Article history:
Received 31 January 2016
Received in revised form 1 May 2016
Accepted 2 May 2016
Available online xxxx

Keywords:
Battery
Graphite
Thin film stress
Delamination
Solid electrolyte interphase

ABSTRACT

Thin film graphite electrodes were investigated in Li half-cells, to investigate the stresses induced by propylene carbonate (PC) additions to a standard liquid electrolyte. *In situ* wafer curvature measurements indicate that substantial compressive stress occurs above 0.5 V, before there is significant Li intercalation into the graphite. Transmission electron microscopy shows that this cycling produces voids throughout the film, via delamination between graphene layers. To explain these observations, a model based on interlaminar debonding and the subsequent buckling of graphite layers is proposed. Existing mechanics models of these phenomena are in good agreement with the experimental observations. Based on this analysis, it appears that the PC additions lead to a very low value of the interlaminar fracture resistance.

© 2016 Published by Elsevier Ltd.

1. Introduction

The solid electrolyte interphase (SEI) films that passivate anodes in Li ion batteries are critically important [1–4]. Because SEI formation consumes Li, it is often a major contributor to decreasing the coulombic efficiency and cycle life of rechargeable batteries. In previous work, we showed that SEI formation on carbon electrodes is accompanied by large, irreversible compressive stresses [5,6]. These studies were all conducted with a standard electrolyte mixture, containing 50% ethylene carbonate (EC) and 50% dimethyl carbonate (DMC). Based on several characterization methods, we proposed that these stresses in the SEI were related to solvent co-intercalation near the graphite surface. However, the degree to which this can occur with the EC/DMC electrolyte is unclear (and somewhat controversial). To better demonstrate that solvent co-intercalation leads to near-surface stresses, the new work presented here is based on adding propylene carbonate (PC) to the electrolyte. This approach is based on a substantial amount of prior work which demonstrates that solvent co-intercalation is more pronounced with PC. ropylene carbonate electrolytes have been used in a variety of systems. In comparison with EC, PC has a number of desirable properties including improved solvation of Li salts, better thermal stability, and a lower melting point. However, it is widely known that PC leads to the degradation of graphite electrodes, primarily via the exfoliation of the active material. This has generally been attributed to the co-intercalation of PC into the graphite structure [7–10]. To improve the compatibility of PC with graphite anodes, prior research has explored variations in the carbon structure (e.g., replacing the standard hexagonal order in graphene sheets with material that has a substantial rhombohedral content) [9]. Other work has also examined modifications to the PC electrolyte chemistry [10,11].

The research reported here uses direct, *in situ* stress measurements to show that PC additions lead to compressive stresses in thin film graphite electrodes, at potentials above 0.3 V where solvent co-intercalation is known to occur. Full exfoliation of the graphite (i.e., loss of active material) was avoided by using relatively small amounts

* Corresponding author.
E-mail address: Brian_Sheldon@brown.edu (B.W. Sheldon).

http://dx.doi.org/10.1016/j.eml.2016.05.001
2352-4316/© 2016 Published by Elsevier Ltd.

Please cite this article in press as: B.W. Sheldon, A. Tokranov, Internal stress due to solvent co-intercalation in graphite electrodes for Li ion batteries, Extreme Mechanics Letters (2016), http://dx.doi.org/10.1016/j.eml.2016.05.001

of PC. Significant changes in the graphite structure were observed with electron microscopy. A basic film buckling analysis was then employed to evaluate the experimental results.

2. Experiments

Graphitic thin film electrodes were produced by chemical vapor deposition (CVD). The synthesis, characterization, and electrochemical cycling behavior for these materials are reported elsewhere [9]. Similar films were used in our previous work with a standard EC/DMC electrolyte, where SEI formation was accompanied by the creation of large compressive stresses [4,5]. For the new experiments reported here, a small amount of PC (5% or 10% by volume) was added to the same electrolyte (1M LiP_6 in EC:DMC (1:1)).

The method used for *in situ* stress measurements is also described elsewhere [12,13]. Fig. 1 shows examples of the voltage and stress data. The stress–thickness value here is obtained from the measured curvature of the substrate, κ, based on the Stoney equation [14]:

$$\sigma_{NOM} h_o = \int_0^h \sigma(z) dz \cong \frac{B_s h_s^2 \kappa}{6} \quad (1)$$

where z is the dimension normal to the film surface, and B_S and h_S are the biaxial modulus and thickness of the substrate. Because the electrode thickness, h, changes during lithiation, it is convenient to describe the results as a nominal stress, σ_{NOM}, based on the initial film thickness, h_o.

Samples for transmission electron microscopy (TEM) were prepared using a standard lift-out procedure that is described elsewhere [5]. Raman spectroscopy with a 532 nm excitation was also used to characterize the carbon structure, before and after cycling. For each measurement, the spectra were obtained by averaging a 10 × 10 array of points, over an area of 100 μm × 100 μm.

3. Results

In Fig. 1 most of the trends observed with PC are qualitatively similar to the stress response observed with the original EC/DMC mixture [4,5]. However, adding PC decreases the overall stress–thickness values that occur during cycling. The TEM images in Fig. 2 also show that the PC additions lead to an extensive network of void space inside of the graphite. It appears that these openings in the material were created by debonding between adjacent graphene layers. This behavior is nominally consistent with prior work showing that PC additions lead to solvent co-intercalation in graphite, which should create significant internal stresses in the graphite. The void formation in Fig. 2 then presumably relaxes some of these stresses.

As seen in Fig. 2(a), the void formation in these films also leads to substantial overall swelling. After one cycle, the thickness more than doubled with 5% PC added and almost tripled with 10% PC added. After multiple cycles the electrode thickness increases further (to almost four times its original thickness after four cycles in 5% PC). The continuing expansion during multiple cycles is consistent with

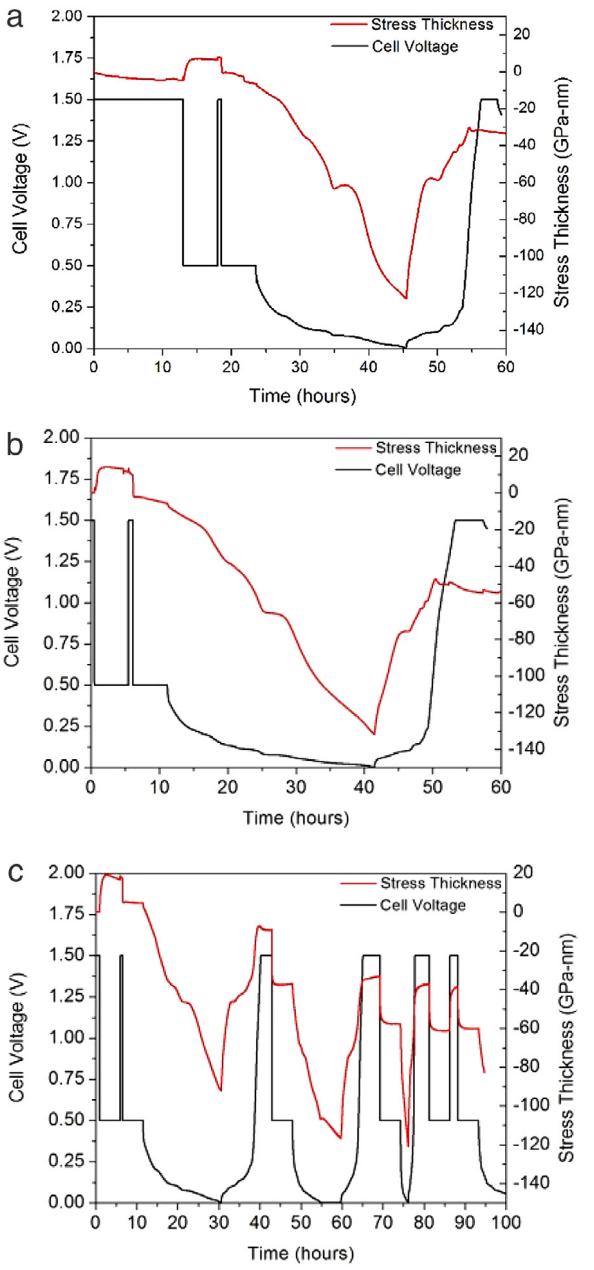

Fig. 1. Cell voltage and stress–thickness during electrochemical cycling: (a) One cycle with 5% PC added; (b) One cycle with 10% PC added; (c) Multiple cycles with 5% PC added.

continuing solvent co-intercalation in these materials, as new surface area is created by void formation. Raman spectra before and after cycling are also shown in Fig. 3. These results show that the local graphite structure is retained, which is consistent with the TEM observations. The reduced peak heights here could be caused by a variety of factors, but they may reflect reduced intensity due to the presence of the internal voids. Another interesting observation is that the interaction between the Raman laser and the carbon causes some disintegration of the film material,

Please cite this article in press as: B.W. Sheldon, A. Tokranov, Internal stress due to solvent co-intercalation in graphite electrodes for Li ion batteries, Extreme Mechanics Letters (2016), http://dx.doi.org/10.1016/j.eml.2016.05.001

Download English Version:

https://daneshyari.com/en/article/5014642

Download Persian Version:

https://daneshyari.com/article/5014642

Daneshyari.com