

## Using Green's Functions to Understand the Stresses on a Li-air Battery Electrode

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### Abstract

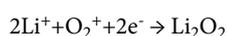
In this work the growth of a Li electrode-electrolyte interface in the presence of an elastic prestress is studied. In particular the focus is on Li-air batteries with a solid electrolyte, LIPON. Theoretical studies and experimental evidence show that during the process of charging the battery the replated lithium adds unevenly to the electrode surface. This eventually leads to dendrite formation as the battery is charged and discharged numerous times. This study focusses on the deviation from flatness of the electrode and the surface Green's function is also developed. It was found that the theoretical formulation is in line with the literature.

**Keywords:** Electrode-electrolyte interface; Li-air batteries; Green's function

### Introduction

A battery is an electrical device that converts chemical energy into electrical energy. As in all electrochemical systems, a battery consists of two electrodes separated by an electrolyte. An external, electronic conductor wire connects the two electrodes and is used as a pathway for electrons to flow and create the electric current. Due to their high energy per unit mass, batteries have received extensive interest in the recent decades. This fact makes their study and development in order to fulfill the demands of current society.

Metal-air batteries are promising candidates for next generation power sources due to their low cost, long shelf life, environmental friendliness, and high energy density [1-3]. A typical nonaqueous Li/O<sub>2</sub> battery is composed of a Li-metal foil (negative electrode), a thin solid lithium-ion conducting electrolyte membrane, and a high surface area positive carbon electrode that is loaded with a catalyst; e.g., Mn, Ni, or Co, for the Li/O<sub>2</sub> reduction at the positive electrode [4-9]. The cell is exposed to the atmosphere at the carbon positive electrode, but is otherwise isolated from the environment. Oxygen from the atmosphere is adsorbed onto the carbon electrode and is reduced in the presence of the Li during battery discharge. The overall reaction is



Lithium compounds are widely used as an electrode material for rechargeable batteries due to their high electropositivity and low weight of lithium metal. During battery operation lithium at the negative electrode gives up electrons to become Li<sup>+</sup> which dissolves into the electrolyte. This process is reversed during the recharge cycle, but the replated lithium adds unevenly to the electrode surface. As the battery is charged and discharged, dendrites have observed to grow from one electrode to the next through the electrolyte [10-14]. Dendrite formation can cause a short-circuit (electrons find an easier path to move through the electrolyte and the voltage difference diminishes to zero) and make the battery useless.

For definiteness this work concentrates on the solid-state electrolyte lithium phosphorus oxynitride (Li<sub>3</sub>PO<sub>4</sub>N) LIPON for short. It is a solid-state electrolyte which is far safer compared to other conventional liquid flammable electrolytes that have been used in the past for lithium ion batteries [15-19]. LIPON is considered to be one of the most promising electrolyte enhanced materials due to its stability and sufficient ionic conductivity.

### The Nearly Flat Electrode-Electrolyte Interface

This work attempts to estimate the dependence of the free-energy of an idealized electrode-electrolyte system on a non-planar profile of the interface. The profile is described as

$$z=h(x,y,t) \quad (1)$$

In this representation, it is assumed the interface is shallow, thus representable as a graph. The profile of the interface is described by means of a height function *h*. In so doing Cartesian axes *x* and *y* span the interface and *z* is traverse to it.

Consider the function *g*

$$g(x,y,z,t)=z-h(x,y,t) \quad (2)$$

Then to leading order in  $|\nabla h|$ , the corresponding unit normal to the interface is given by

$$n = |\nabla g| = \frac{\partial g}{\partial x}e_1 + \frac{\partial g}{\partial y}e_2 + \frac{\partial g}{\partial z}e_3 = -\frac{\partial h}{\partial x}e_1 - \frac{\partial h}{\partial y}e_2 + 1e_3 \quad (3)$$

where *e<sub>i</sub>* is the standard basis.

Whereas the element of area is

$$dA \sim \left(1 + \frac{1}{2}|\nabla h|^2\right) dx dy \quad (4)$$

a planar interface is considered first and then modified to the nonplanar case. In addition to the concentration and electrostatic fields, the planar interface carries along an elastic field. This field is

assumed to be a piecewise uniform and equilibrated prestrain field  $\varepsilon_{ij}^*(x, t)$  and residual stress field  $\sigma_{ij}^*(x, t)$  at zero Li+ concentration.

As a result, in the planar frame, for the electrolyte and solid electrode

$$\varepsilon_{ij}^* = \varepsilon_{ij}^{*E} \quad z > 0, \quad (5)$$

$$\varepsilon_{ij}^* = \varepsilon_{ij}^{*S} \quad z < 0, \quad (6)$$

$$\sigma_{ij}^* = -c_{ijkl}^E \varepsilon_{kl}^{*E} \equiv \sigma_{ij}^{*E} \quad z < 0, \quad (7)$$

$$\sigma_{ij}^* = -c_{ijkl}^S \varepsilon_{kl}^{*S} \equiv \sigma_{ij}^{*S} \quad z > 0, \quad (8)$$

$$\sigma_{i3}^{*E} - \sigma_{i3}^{*S} = 0 \quad z = 0. \quad (9)$$

where  $c_{ijkl}$  is the elastic moduli.

Thus, for the planar interface the elastic field consists of equilibrated constant residual stresses in the electrolyte and the solid electrode.

However, the deviation from the planar profile modifies the elastic field to leading order in  $|\nabla h|$ . The corresponding correction displacement field  $u$  satisfies the problem,

$$\sigma_{ij,j}^S(u) = 0 \quad z < h(x, y, t) \quad (10)$$

$$\sigma_{ij,j}^E(u) = 0 \quad z > h(x, y, t) \quad (11)$$

$$\sigma_{i3}^E(u) - (\sigma_{i\beta}^{*E} + \sigma_{i\beta}^E(u))h_{,\beta} \quad z = (x, y, t) \quad (12)$$

$$\sigma_{ij}^S(u) - (\sigma_{i\beta}^{*S} + \sigma_{i\beta}^S(u))h_{,\beta} \quad z = (x, y, t) \quad (13)$$

$$u_i \rightarrow 0 \quad z \rightarrow \pm \infty \quad (14)$$

where, here and subsequently, Greek indices take values in  $\{1, 2\}$  and

$$\sigma_{ij}^S(u) = c_{ijkl}^S \varepsilon_{kl}^S(u) \quad (15)$$

$$\sigma_{ij}^E(u) = c_{ijkl}^E \varepsilon_{kl}^E(u) \quad (16)$$

In order to fix the geometry, a change of variable is made

$$u_i(x, y, z, t) = v_i(x, y, z - h(x, y, t), t) \quad (17)$$

Two new relations are possible

$$u_{i,\alpha} = v_{i,\alpha} - v_{i,3}h_{,\alpha} \quad (18)$$

$$u_{i,3} = v_{i,3}, \quad (19)$$

or,

$$u_{ij} = v_{ij} - v_{i3}h_{,\beta}\delta_{j\beta} \quad (20)$$

Hence

$$\varepsilon_{ij}(u) = \varepsilon_{ij}(v) - \frac{1}{2}(v_{i,3}\delta_{\beta j} + v_{j,3}\delta_{\beta i})h_{,\beta} \quad (21)$$

and

$$\sigma_{ij}(u) = \sigma_{ij}(v) - c_{ijk\delta}v_{k,3}h_{,\delta}. \quad (22)$$

In this representation, the equilibrium problem becomes, to first order,

$$\sigma_{ij,j}^S(v=0) \quad z < 0 \quad (23)$$

$$\sigma_{ij,j}^E(v=0) \quad z > 0 \quad (24)$$

$$\sigma_{i3}^E(v) - \sigma_{i\beta}^{*E}h_{,\beta} = \sigma_{i3}^S(v) - \sigma_{i\beta}^{*S}h_{,\beta} \quad z = 0 \quad (25)$$

$$v_i \rightarrow 0 \quad z \rightarrow \pm \infty \quad (26)$$

The attendant change in elastic energy is

$$E^{ela} = \int_{\tilde{\sim}} \int_{\tilde{\sim}} \frac{1}{2} G_{ik}(x - x' \tilde{\sim}) \sigma_{i\beta}^* \tilde{\sim} \tilde{\sim} \sigma_{k\delta}^* \tilde{\sim} \tilde{\sim} h_{,\beta}(x) h_{,\delta}(x') dx dx' \quad (27)$$

Where

$$\tilde{\sim} \sigma_{ij}^* \tilde{\sim} = \sigma_{ij}^{*E} - \sigma_{ij}^{*S} \quad (28)$$

Is the jump in the residual stress tensor at the interface, and is the interfacial Green's function?

## Results

Using Mathematica, the Green's function matrix was found.

$$\begin{pmatrix} 2.8050 & -0.64476 & 0.32652i \\ -0.64476 & 2.8050 & 0.32652i \\ -0.32652 & -0.32652i & 2.2303 \end{pmatrix} \quad (29)$$

This matrix is the displacement component in the xi-direction at point x when a unit body force in the xk-direction is applied at point in the infinity extended material. This result is in agreement with the literature [20,21].

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