

## Modeling of Volume Change Behavior of Porous Electrodes

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Electrochemical devices are expected to play a vital role in the future of energy consumption for various purposes ranging from house hold usage to space exploration. Research is being conducted on various aspects so as to improve the design and operating range of these devices and one of the primary focuses is the porous electrode<sup>1,2</sup>. It has been reported that there is significant volume change during electrode processes, within the porous electrodes and depending on the material it can be as high as, but not limited to 300%. These large volume changes along with product formation in pores can cause severe mechanical and performance degradation<sup>3</sup>. Prediction of stresses generated inside the electrode could give crucial insight into design parameters, lately diffusion induced mechanical stresses for electrode particles has recently attracted a significant interest in electrochemical research field<sup>4-6</sup>. Here we have formulated a continuum presentation of the porous material which combines mechanics of the solid phase of the porous material with the dependence of porosity on stress, as in rock-mechanics.

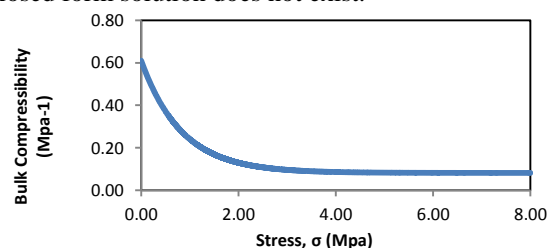
Using the material balance equation and the porosity constitutive law, we have developed a volume averaged formulation that relates the volumetric strains to the porosity and the current as:

$$(1 + \varphi) \frac{\partial(1-\varepsilon)}{\partial t} + (1 - \varepsilon)(1 + \varphi) \frac{\partial \varphi}{\partial t} = \beta I$$

where  $\varepsilon$ ,  $\varphi$ ,  $\sigma$ ,  $I$  are porosity, volumetric strain, and confining pressure, and current, respectively. This is an extension to the previously design dependent swelling coefficient<sup>3</sup>. This new model facilitates the perdition of volume and porosity change without having the design geometry information in advance.

In rock mechanics the deformation of the porous rock during the application of stress is characterized by its bulk compressibility<sup>7</sup>, using this and the analogy between thermal stress-strain relationships and stress-strain relationship for existing concentration<sup>5</sup>

gradients, a constitutive law is developed for the volumetric strain of the electrode during lithiation. The bulk compressibility data of the electrode that is required has to be obtained experimentally for this model. A typical bulk compressibility and stress behavior is shown in Fig. 1. Using this newly developed stress-strain relationship, the change in porosity during lithiation, can then also be predicted. The above model is general and in conjunction with appropriate boundary and initial conditions, it can be used to predict the volume change of any electrode. To demonstrate its applicability, this formulation was applied to a three-dimensional confined rectangular electrode that undergoes swelling during operation. Due to the nonlinear nature of the equation, the closed form solution does not exist.



**Fig. 1:** A typical bulk compressibility behavior of the porous rock under stress.

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