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Featured Letter

Effective modulus of graphite electrode in Li-ion battery by considering ion concentration, porosity, and binding energy during lithium intercalation

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A B S T R A C T

A new mathematical method that considers the influences of Li-ion concentration, Li—C binding energy, and porosity simultaneously in an electrode is suggested for predicting the effective elastic modulus (EEM) of an electrode. EEMs of electrodes are significantly influenced by the porosity and ion concentration. Graphite electrodes are fabricated and tensile tests are conducted at various states of charge by constructing some pouch cells with $LiMn_2O_4$ cathode and graphite anode. EEM of graphite increases dramatically during Li-ions' intercalation into the electrode, and reaches a value up to 3 times that of the uncharged electrode. The experimental results are compared with analytical predictions to validate, and the two results show good agreement with a maximum error of 8.6%.

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1. Introduction

The Li-ion battery is widely used due to its superior performance, such as high capacity and energy density. Porous materials such as graphite are widely used as anode materials [1]. Due to that Li-ions intercalate into the layered graphite during charge and de-intercalate during discharge, the volume and porosity of electrodes change, causing fracture or delamination of the electrodes [2]. Consequently, the capacity of battery is degraded. Recently, the mechanical properties of electrodes have been investigated to improve the performance of batteries by avoiding fatigue of electrodes during lithium intercalation and de-intercalation [3–5]. The volume of the graphite electrode increased by 10% during ion intercalation (Li → LiC_6) [6].

The combined influence of changes in the porosity, Li-ion concentration and binding energy between intercalating ions in the electrodes were not considered, although only ion concentration was investigated in several papers. In order to predict the EEM of electrodes accurately, a new functionally coupled relation has been developed. It aims to illustrate the relationship between the elastic modulus and ion concentration of electrodes, in addition to the influences of porosity and binding energy of Li—C chemical compound.

2. Formulation

2.1. Li-ions and porosity

The 2D Li-ion battery with cathode, anode, and separator (Fig. 1(a)) is modeled to simulate the transport of Li-ion and to capture the corresponding porosity variations in electrodes and lithium concentration by using COMSOL Multiphysics. $LiMn_2O_4$ and graphite are cathode and anode, respectively. The electrolyte is composed of $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with the volume ratio (EC/DMC = 1/2). The initial Li-ion concentration is 2.45×10^4 mol/m^3 (saturated) for the graphite electrode. The parameters used for analyses are summarized: for graphite, electrical conductivity (S/m) = 100, diffusion coefficient $(cm^2/s) = 1.12 \times 10^{-10}$ [7] (although this depends on the intercalation level [8]), density (kg/m^3) = 2270, state of charge = 1, initial porosity of delithiated electrode = 0.69; for $LiMn_2O_4$, electrical conductivity (S/m) = 3.8, diffusion coefficient$(cm^2/s) = 1.3 \times 10^{-14}$ [9], density (kg/m^3) = 4140, equilibrium potential (V) = 4; for $LiPF_6$, diffusion coefficient $(cm^2/s) = 7.5 \times 10^{-7}$, electrical conductivity (S/m) = 1.1, electrolyte salt concentration (mol/m^3) = 1000.

From Fig. 1(b) and (c), it is observed that Li-ions initiate diffusing from anode and intercalate into cathode during discharge. As Li-ions intercalate, the electrode porosity decreases while increasing the state of charge (SOC). The continuously decreasing porosity is due to the intercalation of Li-ions into porous space of electrode.

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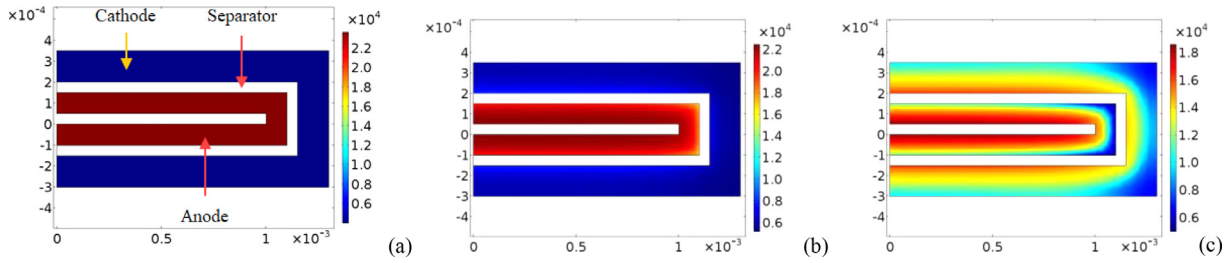   *E-mail address:* kimchul@knu.ac.kr (C. Kim).

Fig. 1. Model of (a) 2D Li-ion battery (unit: mm) and migration of ions during discharge at (b) 100 s and (c) 1000 s.

The lithium concentration is also called as SOC [3]. As the Li—C chemical compound forms due to the intercalation, its porosity decreases from 0.69 to 0.39 in this analysis. The relationship between porosity and SOC can be obtained from the analysis data, as shown in Fig. 2(a) and Eq. (1).

$$P = -0.5755s^2 + 0.2166s + 0.6716 \tag{1}$$

where s is the SOC of a battery and P is the porosity of electrode.

2.2. Effective modulus

As more Li-ions intercalate, the porous electrodes are partially filled. Consequently, the volume fraction of Li—C chemical compound increases, resulting in a decrease in the porosity of the electrode. It not only affects the electrode modulus, but also determines the durability and capacity of a lithium battery [10].

An effective modulus (E) of particulate composites is proposed as Eq. (2) using the differential effective medium approach [11] and the shear and bulk moduli of spherical particles [12]. This equation can consider the volume fractions of three phases (i.e., particles, polymer matrix (binder), and pore space).

$$\frac{E}{E_m} \cdot \left[\frac{x_1 E_m - 3E_d(x_2 + x_3)}{x_1 E - 3E_d(x_2 + x_3)} \right]^{(x_4 + 53/46)}$$
$$\times \left[\frac{x_1 E - 3E_d(x_2 - x_3)}{x_1 E_m - 3E_d(x_2 - x_3)} \right]^{(x_4 - 53/46)}$$
$$= [1 - (\varphi_p + \varphi_m)]^{-2.5} \tag{2}$$

$$x_1 = 46(1 - v_d)(1 - 2v_d), \ x_2 = 4 - 23 \cdot v_d$$

$$x_3 = \sqrt{69 v_d^2 - 414 v_d + 246}, \ x_4 = (833 - 736 v_d)/46 \cdot x_3$$

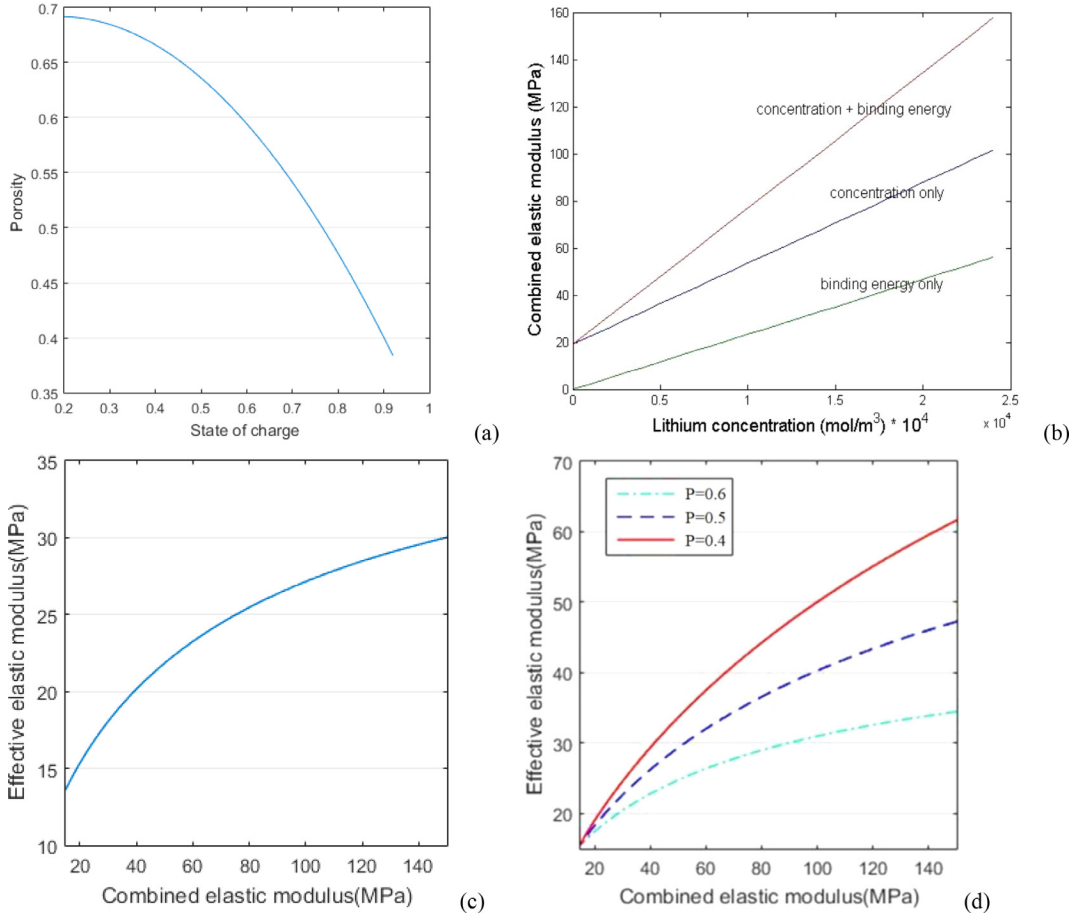**Fig. 2.** (a) Porosities at various charges, (b) E_d with various Li-ion concentration, (c) E vs. E_d, and (d) with changing porosity.