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The Effects of Microstructure on Electrochemical Properties of Porous Electrodes

전기화학적 물성에 미치는 다공성 전극의 미세구조의 영향

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Porous structure is omnipresent in Nature. It is the basic structure of life and universe, providing large surface area in a space-saving way. Microstructure of porous materials has been characterized by various analytical methods. Previous methods, however, are non in situ techniques for the electrochemical applications, so that measured structures may not be identical to those accessible to electrolyte ions in real applications. Therefore, it has been extremely difficult to correlate the microstructure of porous electrodes with electrochemical behavior of energy storage devices.

Here we present the electrochemical porosimetry (ECP) giving microstructural information most meaningful in electrochemical systems. The methodology is based on the transmission line model with pore size distribution (TLM-PSD) that relates electrochemical impedance with microstructure such as pore size distribution (PSD) and pore length (l_p). The total impedance of a porous electrode was described as a vector summation of impedances for each electrochemical pathways with a distribution density function. The resultant governing equation of TLM-PSD has three fitting parameters (Y_p , α_{μ_0} , σ) in the complex nonlinear least square (CNLS) fitting procedure. Y_p is the total ionic conductance through pores. The representative penetrability coefficient α_{μ_0} means the effectiveness for utilizing surface of porous structures. σ is the width of distribution of penetrability or PSD. Under conditions that the geometric factors affect the frequency dispersion of a porous electrode dominantly, the fitting parameters lead to the concrete geometric parameters (r_{μ} , σ , l_p) specifying the PSD, where r_{μ} , the mode radius at which a distribution function gives the maximal value; σ , distribution width of PSD; l_p , average pore length or electrochemical pathway.

This geometric information was validated for the microporous, mesoporous and macroporous samples. Also, the ECP could be used as a nondestructive probe to investigate the construction of electrochemical devices.