

리튬이온전지에 실리콘 상용화 기반 마련

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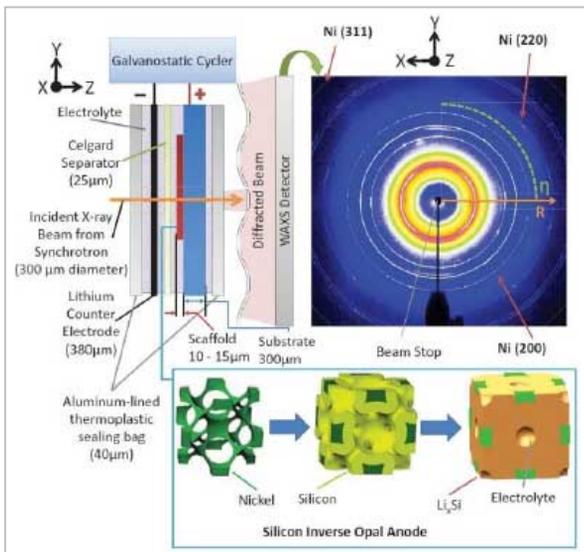
연구내용

미국 일리노이대, 노스웨스턴대, 아르곤 연구소와의 공동연구를 통해 리튬이온 충방전시 실리콘(Si)의 3차원 나노 금속틀에 작용하는 응력과 변형과의 상관 관계를 밝혀 이를 정량화하는데 성공하였다. 리튬이온전지의 음극소재로 각광받고 있는 실리콘(Si)은 리튬이온 충방전시에 발생하는 부피변화로 인해 상용화에 어려움을 겪어 왔다. 그러나 이러한 부피변화에 따른 변형률 및 응력변화를 정량화 하는 방법이 개발됨에 따라 리튬이온전지에서 실리콘을 음극소재로 상용화 할 수 있는 기반이 마련되었다.

기대효과

이번 연구는 주사전자현미경, 투과전자현미경, 원자현미경 등을 이용하여 재료의 표면에 발생하는 변형만을 분석하는 기존의 연구방법에서 탈피하여 복잡한 구조의 시료 내부에서 발생하는 전체적인 변형까지 분석할 수 있는 '입자가속기(Synchrotron)를 이용한 X선 회절법(X-ray diffraction)'을 활용하여 연구에 성공할 수 있었다.

이번 연구에 사용된 '입자가속기(Synchrotron)를 이용한 X선 회절법(X-ray diffraction)'은 반도체 및 세라믹 등의 신소재분야 뿐만 아니라 환경소재, 나노바이오 융합소재 및 의료, 진단 분야에 이르기까지 폭넓은 연구분야에서 활용될 수 있을 것으로 전망된다.



[그림 1] 입자가속기 XRD를 활용한 실리콘 리튬이온전지 결정구조 분석 모식도

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In Operando Strain Measurement of Bicontinuous Silicon-Coated Nickel Inverse Opal Anodes for Li-Ion Batteries

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Elastic strains are measured in operando in a nanostructured silicon-coated nickel inverse opal scaffold anode, using X-ray diffraction to study the Si [d₀₁] lithiation-induced Ni strains. The volume expansion upon lithiation of the Si in the anode is constrained by the surrounding Ni scaffold, causing mismatch stresses and strains in the Si and Ni phases during cycling. The Ni strains are measured in operando during (dis)charge cycles, using diffraction peak position and peak broadness to describe the distribution of strain in the Ni. During lithiation, compressive strains in the Ni first increase linearly with charge, after which a gradually decreasing strain rate is observed as the maximum lithiation state is approached; upon delithiation a similar process occurs. In-plane average compressive strains on the order of 990 ± 40 με are measured in the Ni scaffold during lithiation, corresponding to compressive stresses of 215 ± 9 MPa. The decreasing strain rates and decreasing maximum and recovered strains suggest that plasticity in Ni and/or Si, as well as delamination between Ni and Si, may occur during cycling. Rate sensitivity in capacity is correlated with strain and a maximum Ni compressive stress of 230 ± 40 MPa is measured at the maximum state of lithiation.

and other applications.¹⁻⁶ Alloying anode materials, such as silicon, are very promising because of their high gravimetric energy densities (up to 3580 mAh g⁻¹ for Si⁰ as compared to graphite (up to 372 mAh g⁻¹ for C)⁷ and the high abundance of Si, but silicon suffers from very high volume changes (>300%) during lithiation.⁸ These volume changes can generate very large stresses, which lead to the delamination, cracking, and pulverization of Si based anodes, ultimately causing rapid capacity fading. The fundamental nature of this volume change process associated with alloying has been well explored in the literature by employing *in situ* scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM), as well as atomistic simulations and theoretical calculations.⁹⁻¹¹ Some *in operando* studies¹²⁻¹⁴ have explored this lithiation-induced expansion during cycling for simple anode geometries, limited in part by the amorphous nature of the alloying mechanism and the difficulty of designing *in operando* experiments. Only these studies have employed galvanostatic cycling methods, which may be more representative of future applications.¹⁵⁻¹⁸

To investigate lithiation strains in Si during cycling, some *in situ* and *in operando* studies have been performed for simple geometries.¹⁹⁻²¹ These studies have employed AFM, TEM and optical laser measurement techniques to measure strains, with AFM and TEM techniques also able to characterize morphology and identify fracture. AFM and TEM studies are able to identify plasticity, cracking and failure occurring in operando and can estimate critical stresses and sites for nanowires, nanoparticles, and other shapes.²²⁻²⁴ These *in situ/operando* studies are effective for describing lithiation stresses and strains that exist on surfaces or anodes with simple geometries but cannot directly measure the spatial distributions of strain that may exist in more complex geometries and structures as well as at buried interfaces, especially for technologically or commercially relevant anode geometries.

X-ray diffraction (XRD) based strain measurements are able to directly measure elastic strain distributions in arbitrary geometries, bulk materials and buried interfaces between different phases or materials in a sample that might not be easily accessible *in situ/operando* otherwise. XRD has been used effectively to describe average strains, strain distributions,

1. Introduction

Lithium ion batteries (LIBs) represent an efficient and modular energy storage solution for a wide variety of portable applications but will require substantially higher energy densities and shorter charging times to meet emerging demand for electric vehicles

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