



Full paper

Diffusion kinetics governing the diffusivity and diffusion anisotropy of alloying anodes in Na-ion batteries

Jun-Hyoung Park^{a,1}, Yong-Seok Choi^{a,1}, Young-Woon Byeon^a, Jae-Pyoung Ahn^b, Jae-Chul Lee^{a,*}^a Department of Materials Science and Engineering, Korea University, Seoul, 02841, South Korea^b Advanced Analysis Center, Korea Institute of Science and Technology, Seoul, 02792, South Korea

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ABSTRACT

Diffusion in alloying anode materials was previously viewed as solute diffusion in conventional alloys. However, solute diffusion, neglecting the presence of a thin intermediate reaction layer between the unreacted anode material and inflowing carrier ions, is insufficient to account for the diffusion kinetics in alloying anodes and their influence on the electrochemical properties of batteries. Here, by performing a comparative study on Na-Sb and Na-Sn battery systems displaying differing diffusion kinetics, we establish the relationship between diffusion kinetics and electrochemical properties for batteries. *In situ* microelectrochemical experiments show that sodiation in Na-Sb and Na-Sn systems is governed by an interface-controlled reaction (ICR) and a diffusion-controlled reaction (DCR), respectively, causing them to display significantly different diffusion rates, diffusion anisotropy, and possibly self-limiting diffusion of carrier ions. Density functional theory calculations are performed to elucidate the structural origin of the observed diffusion behaviors. It is found that the different degrees of structural stability evaluated for the propagating interfaces of the two systems are responsible for the differing diffusion kinetics, which in turn determine the respective diffusion rates and diffusion anisotropy of the anode materials. The present study provides crude yet quantitative guidelines for selecting battery materials and can be used to develop fast-charging batteries with high stability and improved cycle life.

1. Introduction

Unlike solid-state diffusion in conventional alloys, where their crystallinity is retained during solute diffusion, the diffusion of carrier ions into alloying anodes is accompanied by disruption of the crystal structures of anode materials [1–3]. Furthermore, contrary to the direct diffusion of solute atoms into the host crystal lattices of alloys, the diffusion of carrier ions into alloying anodes proceeds indirectly through a thin amorphous intermediate reaction layer located between the unreacted anode material and inflowing carrier ions. This diffusion process in alloying anodes is often referred to as two-phase diffusion and determines the electrochemical performances of batteries [4]. Despite the all-important significance of this two-phase diffusion process, the kinetics and mechanisms governing these behaviors remain unclear.

Owing to the presence of an amorphous intermediate reaction layer, the diffusion kinetics of alloying anodes is determined by the relative magnitudes of the diffusion rates of charge carriers measured at the propagating interface (v_i) and trailing bulk regions of the intermediate reaction layer (v_b) [5,6]; for a battery system with $v_b > v_i$, the entire

diffusion process is governed by v_i (this is termed an interface-controlled reaction, ICR). On the other hand, when v_i is greater than v_b , diffusion is controlled by v_b (termed a diffusion-controlled reaction, DCR). Based on this perspective of diffusion kinetics, extensive studies were performed on alloying anodes, mostly on the Li-Si system [1,7]. For the Li-Si system, v_i is much smaller (by ~15 orders of magnitude) than v_b , rendering the entire diffusion process to be controlled by an ICR. ICR diffusion has also been observed in various battery systems, including Na-Si, Na-P, and Na-Sb. As shown in Table 1, these systems display comparatively slow diffusion rates [8–11], anisotropic diffusion [2,12–16], and shallow penetration depths of carrier ions [7,17], characterizing slow charging rates, short cycle lives, and reduced energy capacity of batteries. In contrast to battery systems governed by ICR, some systems obey diffusion kinetics controlled by DCR (Table 1). For these systems, carrier ions tend to diffuse to anode materials at comparatively rapid rates to greater penetration depths. Furthermore, anode materials expand/swell isotropically during the entire diffusion process, which alleviates stress-induced pulverization of anode materials and improves their cycle life and capacity.

* Corresponding author.

E-mail address: jclee001@korea.ac.kr (J.-C. Lee).¹ These authors contributed equally to this work.