



Full paper

In-situ electron microscopy observation of electrochemical sodium plating and stripping dynamics on carbon nanofiber current collectors

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ABSTRACT

Sodium metal holds promise as the ultimate anode for high-energy-density Na battery systems. Recent progress has been made in terms of rational design of nanostructured 3D current collectors for dendrite-free Na deposition with limited dimensional changes during cycling. However, critical information such as Na nucleation and growth behavior on these hosts remains elusive. Herein, by using amorphous carbon nanofibers (CNF) as a current collector, we present the first nanoscale-resolution observation of electrochemical Na plating/stripping dynamics via in situ electron microscopies. With the use of solid electrolyte, Na metal was found to grow and dissolve reversibly as nano/micro-particles at all the possible locations around individual CNFs and even throughout their network. Notably, inter-fiber Na ion transport was experimentally confirmed, which enables more homogeneous Na deposition deep into the network interior without interfacing the electrolyte; this would be crucial for dendrite-free Na plating, especially in all-solid-state Na batteries. In addition, through a delicately designed in-situ experiment, the CNF interior exhibited a superior Na capacity compared to its graphitized counterpart. Thus, owing to both exterior and interior Na storage of each fiber, CNFs could be a promising host material for building rechargeable composite Na metal anodes with ultrahigh capacity.

1. Introduction

Over the past years, sodium ion batteries (SIBs) have regained increasing attention as a promising alternative to Li ion batteries (LIBs) owing to the unlimited abundance of Na resources and their great potential in future large-scale energy storage applications [1,2]. One of the most challenging issues toward the commercialization of SIB technologies is to develop high-performance anodes capable of hosting sufficient sodium ions. Graphite, the commercialized LIB anodes, however, has proven to be inefficient in Na ions storage due to the relatively larger radius of Na⁺. Hence, intense research efforts have recently focused on the exploitation of alternative anode materials, including disordered carbons, Group-IV elements like Si, Ge, Sn and various metallic compounds, etc [3,4]. In theory, among all the anode candidates, metallic Na holds the greatest potential as it has the highest specific capacity (1166mAh/g) and the lowest electrochemical potential for a sodium anode (−2.71 V vs. standard hydrogen electrode) [5,6]. Furthermore, sodium metal can be matched with Na-free cathodes to achieve high-energy-density battery systems, such as Na–S, Na–O₂ [7–11].

Despite the potential as the ultimate anode for Na battery systems, some major hurdles severely prevent Na metal anodes from practical applications, such as uneven metallic deposition, dendritic growth, and infinite relative dimension change upon cycling, etc. To address the problems, the strategies in terms of rational design of a host for Li/Na deposition have been recently proposed [5,6,12–18], including various 3D carbon matrices or networks (as depicted in Fig. 1b for example) as a mechanically stable skeleton and current collector with good conductivity and large surface area. Due to the substantially reduced areal current density, the carbon-Na composite anodes can effectively ensure uniform Na nucleation and restrict the volumetric change, thus significantly improving the Coulombic efficiency and cycling performance. A full cell constructed with such anode architecture can achieve energy densities of ~400 Wh/kg, far beyond those of SIBs and even the commercialized LIB technology [5].

However, the interaction dynamics between nucleated Na metal and the underlying carbon hosts during electrochemical plating and stripping is largely unknown. In particular, the detailed roles of these carbon scaffolds in Na ion transport and homogeneous deposition have remained unexplored. To gain new insights in understanding the above

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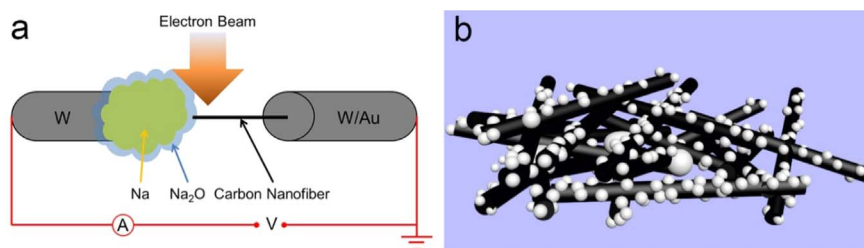


Fig. 1. Schematic illustrations of (a) the in-situ Na battery experimental setup and (b) CNF-Na composite anode comprised of a CNF network and embedded Na depositions.

issues, the direct nanoscale-resolution observation of Na plating/stripping process on current collectors is highly desired, which, to the best of our knowledge, has so far been lacking. Besides, solid electrolytes, the promising candidate of next-generation electrolytes in metal batteries, were rarely used for in-situ observation of alkali metal electrodeposition/dissolution [19]. Compared to the liquid counterparts, the local environment of solid electrolyte/current collector interfaces may change significantly, resulting in new and different metal deposition behaviors that deserve further in-situ investigations.

In this work, we present the real-time visualization of Na plating/stripping electrochemical behaviors on individual carbon nanofibers (CNFs) and their network by constructing an all-solid-state nanobattery inside a transmission electron microscope (TEM) and a scanning electron microscope (SEM) respectively. The combined use of these two in-situ microscopies enables a more thorough structural characterization of both interior and surface of the object during the reaction processes. Such in-situ observations are helpful for us to clarify some crucial issues related to Na deposition/dissolution as follows: (1) what is the morphology and spatial distribution of the Na deposits on nanostructured carbon current collector with a solid electrolyte; (2) how is it possible for uniform, extensive and reversible Na deposition to be achieved in a CNF network with its interior having no contact with the solid electrolyte; (3) how to further improve the Na storage capacity of the CNF-Na composite anode with an optimized design of the anode architectures/microstructures. The present work could enrich our understanding of above issues and inspire new paths in design of high-performance Na metal anodes.

2. Experimental section

Carbon nanofibers used in the work were synthesized by a simple

and scalable electrospinning method [20]. As-prepared CNFs are typically 100–200 nm in diameter and exhibit porous structures in the amorphous carbon matrix. As schematically illustrated in Fig. 1a, a typical nanobattery setup consists of a CNF as the current collector, sodium metal as the counter electrode, and naturally grown Na₂O layer as the solid electrolyte. Such open-cell experimental setups were constructed inside a TEM (Jeol 2100) by using a STM holder (PicoFemto) [21], and in a SEM (Zeiss Sigma) equipped with micromanipulators (Kleindiek) respectively [22]. Once the contact between a CNF and Na₂O layer was established, a constant bias of $-3\text{V}/3\text{V}$ was applied to the CNF against Na metal to initiate the plating/stripping processes (see Supporting information for more experimental details).

3. Results and discussion

Sodium electrodeposition experiments were first performed in the SEM using an Inlens detector for secondary-electron imaging. A frequently observed case of Na deposition is the sphere-like particles that nucleate at the interface between a CNF and Na₂O electrolyte and grow up to microns in size, as documented in Fig. 2a–d. Prior to Na deposition, the pristine CNF was first sodiated, followed by Na saturation at the CNF end, which initiated the subsequent particle nucleation (Fig. 2a). Noticeably, during the expansion of the ball-like particle, the outer layer with a brighter contrast broke into smaller pieces floating on the expanding ball surface, just like the continental drift on Earth's surface (see Supporting Information Movie S1). This floating layer is supposed to be sodium oxide due to the surface oxidation of the Na particle with the trace amounts of oxygen residual in the SEM chamber (and in TEM column as well). Because of the charging effect [23], the insulating oxide layer shows a brighter contrast (compared with Na metal) under SEM imaging, as denoted by the white arrows in Fig. 2b.

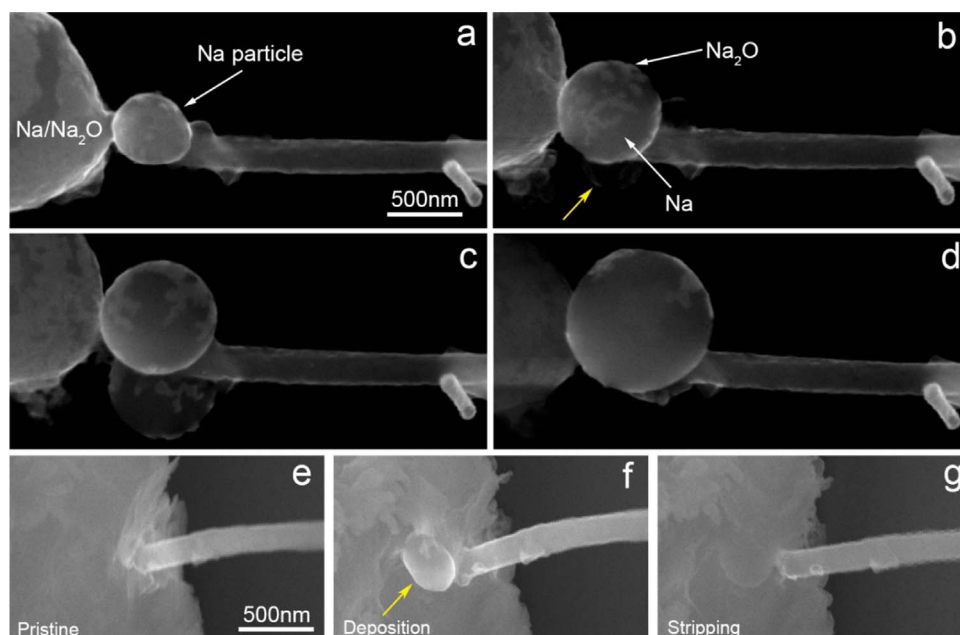


Fig. 2. In-situ SEM observation of the structural evolution of the particles at the interface of CNF/Na₂O electrolyte. (a–d) The expansion and fusion of sphere-like Na particles during a plating process. The yellow arrow in b indicates a new particle that just appears below the former one. (e–g) A typical case of particle deposition and dissolution at the CNF/electrolyte interface during a plating/stripping cycle.

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