



Zirconium-based metal–organic frameworks/porous carbon hybrids as high-performance anode materials for highly stable lithium- and potassium-ion batteries

Michael Ruby Raj^{a,1}, Prakash Krishnaiah^{b,1}, Jinhyuk Baek^a, Byong-Hun Jeon^{b,*}, Gibaek Lee^{a,*}

^a Advanced Energy Materials Design Lab., School of Chemical Engineering, Yeungnam University, Gyeongsan-Si 38541, Republic of Korea

^b Department of Earth Resources & Environmental Engineering, Hanyang University, 222-Wangsimni-ro, Seongdong-gu, Seoul 04763, Republic of Korea

ARTICLE INFO

Keywords:

Metal-organic frameworks
Porous carbon
Potassium-ion batteries
Lithium-ion batteries
Zirconium

ABSTRACT

Metal-organic framework (MOF)-derived carbon materials have been widely investigated as advanced electrode materials. However, post-synthetic modifications suffer from certain limitations in morphology, surface area, and pore size control. Herein, we report a simple strategy to synthesize surface-confined Zirconium(Zr)-based MOF UiO-66-NH₂ carbon hybrids (Zr-MOF@C; denoted as Zr-MOF, Zr-MOF@C10, Zr-MOF@C25, and Zr-MOF@C50) through a covalent assembly/amide linkage between the MOFs and hierarchical porous carbon (PC) in various proportions under solvothermal conditions. Zr-MOF@C hybrids have been utilized as the anode materials for lithium- (LIBs) and potassium-ion batteries (KIBs). In LIBs, the Zr-MOF@C10, Zr-MOF@C25 and Zr-MOF@C50 anodes delivered the discharge capacities of 126, 65 and 94 mA h g⁻¹ at 100 mA g⁻¹ after 100 cycles, respectively. In KIBs, the Zr-MOF@C10 and Zr-MOF@C25 exhibited the high discharge capacities of 78 and 70 mA h g⁻¹ at 100 mA g⁻¹ over 100 cycles. In addition, the Zr-MOF@C25 and Zr-MOF@C50 anodes exhibited an outstanding rate capability with a reversible capacity of ~166 mA h g⁻¹ vs. K/K⁺ and 176 mA h g⁻¹ for Li/Li⁺, respectively, while well-maintained long-term cyclic stabilities of ~57 mA h g⁻¹ (Zr-MOF@C25 vs. K/K⁺) and ~140 mA h g⁻¹ (Zr-MOF@C50 vs. Li/Li⁺) at 1 A g⁻¹ over 1000 cycles. The electrochemical kinetics studies revealed that Li⁺ and K⁺ storage efficiencies of all anodes were dominated by a surface-charge capacitive effect and diffusion-driven charge storage mechanism, respectively. These findings provide new insights for designing high-performance surface-confined MOF-based carbon composite materials for next-generation high-energy storage devices.

1. Introduction

Recently, lithium-ion batteries (LIBs) with fast charging performance have become vital in various portable energy storage systems and the electric vehicle industry, owing to their large voltage window, high energy density, and long cycle life with sufficient energy [1–3]. Potassium-ion batteries (KIBs) have also been developed as energy storage systems owing to their low cost, high cell voltage, high energy density, similar electrochemical properties of potassium to those of lithium, and the availability of potassium [4]. However, these batteries still have the limitations of charging efficiency, rate capabilities, long-life cycling stability, considerably slower K⁺ diffusion kinetics (due to the larger ionic radius of K⁺ (~1.38 Å) than that of Li⁺), and safety for

practical applications. Therefore, the design of novel electrode materials with wide sources and environmental friendliness to achieve excellent electrochemical performance in both LIBs and KIBs is challenging.

Metal-organic frameworks (MOFs), a special class of porous materials with unprecedented physicochemical properties and structural stability, have flourished as ideal platforms for constructing advanced electrode materials for various rechargeable batteries because of their highly interconnected pores, large surface areas, coordinatively unsaturated redox-active sites, and intrinsically porous structures that enable rapid electrolyte penetration/ion diffusion and fast mass transportation [5,6]. However, several pristine MOFs suffer from poor conductivity, low mechanical strength, limited functionality, and irreversible structural degradation during charging-discharging, hindering their direct

* Corresponding authors.

E-mail addresses: bhjeon@hanyang.ac.kr (B.-H. Jeon), gibaek@ynu.ac.kr (G. Lee).

¹ These authors have contributed equally to this work.