



Highly stable P'3-K_{0.8}CrO₂ cathode with limited dimensional changes for potassium ion batteries

Nirmallesh Naveen^a, Su Cheol Han^a, Satendra Pal Singh^b, Docheon Ahn^c, Kee-Sun Sohn^{b,**}, Myoung-ho Pyo^{a,*}

^a Department of Printed Electronics Engineering, Sunchon National University, Chonnam, 57922, South Korea

^b Faculty of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul, 05006, South Korea

^c Beamline Division, Pohang Accelerator Laboratory (PAL), Pohang, 37673, South Korea

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ABSTRACT

O3-KCrO₂ is the only known stoichiometric layered transition metal oxide with a layered structure, which enables efficient coupling with a graphite anode for K⁺-shuttling batteries. O3-KCrO₂, however, shows low Coulombic efficiency during 1st charge/discharge cycle and continuous capacity fading during subsequent cycles. Here, we present a slightly K⁺-deficient compound P'3-K_{0.8}CrO₂, synthesized from a commercially available K₂CrO₄, as a stable cathode in potassium ion batteries. During the 1st charge, K_{0.8}CrO₂ mostly retains its P'3-phase with a short P3 region and finally returns to a P'3-phase (K_{0.48}CrO₂). Subsequent discharge shows reversible phase transitions, but ultimately yielded a new O'3-K_{0.9}CrO₂ phase. Absence of an O3-phase and persistence of a P'3-phase during charge/discharge, result in negligible volume changes (1.08%) and facile K⁺-diffusion through the spacious-prismatic sites ($D = 10^{-11} - 10^{-10} \text{ cm}^2 \text{ s}^{-1}$). This eventually contributes to a significant improvement in cyclic stability (99% retention after 300 cycles at 1 C) and rate capability (52 mAh·g⁻¹ at 2 C), respectively. We believe that the use of slightly K⁺-deficient chromium oxides synthesized via a simple protocol should enhance the commercial viability of K_xCrO₂ in potassium ion batteries.

1. Introduction

Rechargeable batteries now play dual roles in green energy societies. In one way, they act as energy storage devices for transient natural energy sources, but also act as power devices for portable electronics and electric vehicles [1–3]. Currently, lithium ion batteries (LIBs) are the predominant choice for these purposes due to their superior energy density and long cycle-life [4]. Limited reserves and the inhomogeneous distribution of lithium emphasize the necessity to develop alternative rechargeable battery systems. In due course, sodium and potassium ion batteries have been chosen as promising candidates because of their crustal abundance and physico-chemical properties that are identical to those of lithium [5–7]. Despite the discovery of numerous Na-ion conducting cathodes, however, a lack of a reliable anode material is considered as a major barrier in realizing commercial sodium ion batteries (NIBs) [8–10]. Of course, there are few candidates possessing the excellent electrochemical properties as NIB anodes [11–13]. For

example, hard-carbon was recently addressed to have a long cycle-life and a reasonable capacity in an ether-based electrolyte [11]. To attain commercial reliability/viability as graphite in LIBs, however, more studies seem to be required. Potassium ion batteries (KIBs) have benefits over NIBs that include a relatively lower standard reduction potential ($E^0 [\text{K}/\text{K}^+] = -2.94 \text{ V}$ vs. $E^0 [\text{Na}/\text{Na}^+] = -2.73 \text{ V}$ vs. SHE) and a higher level of ion mobility (10.7 mS cm^{-1} for K⁺ vs. 9.7 mS cm^{-1} for Na⁺ in carbonates) [14–16], but such advantages are rather trivial. The biggest virtue of KIBs is that graphite can reversibly accommodate K⁺ ions, which allows a narrowing of the research focus to the development of K⁺-conducting cathode materials [17–19].

Expectation of high specific capacity and fast solid-state ionic diffusion led to the examination of layered potassium transition metal (TM) oxides for use as KIB cathodes [20]. The synthesis of stoichiometric compounds (KTMO₂), however, was not successful due to strong K⁺-K⁺ repulsion. Instead, non-stoichiometric layered K_xMnO₂ ($x = 0.3$ and 0.5) [21,22], K_xCoO₂ ($x = 0.4$ and 0.6) [23,24], and K_{0.7}Fe_{0.5}Mn_{0.5}O₂ [25]

* Corresponding author.

** Corresponding author.

E-mail addresses: kssohn@sejong.ac.kr (K.-S. Sohn), mho@sunchon.ac.kr (M. Pyo).

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