

High-Capacity Sodium Peroxide Based Na–O₂ Batteries with Low Charge Overpotential via a Nanostructured Catalytic Cathode

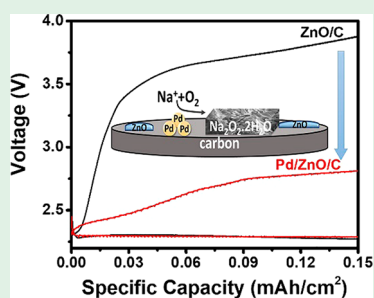
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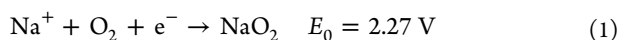
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S Supporting Information



ABSTRACT: The superoxide based Na–O₂ battery has circumvented the issue of large charge overpotential in Li–O₂ batteries; however, the one-electron process leads to limited capacity. Herein, a sodium peroxide based low-overpotential (~0.5 V) Na–O₂ battery with a capacity as high as 7.5 mAh/cm² is developed with Pd nanoparticles as catalysts on the cathode.

Rechargeable metal–air batteries, especially the non-aqueous Li–O₂ batteries, are recognized as one of the most promising techniques for next-generation energy storage owing to their high theoretical specific energy.¹ However, one of the biggest challenges facing the Li–O₂ battery is the large charge overpotential, which results in low round-trip efficiency and poor cycle life.² Therefore, an efficient oxygen evolution reaction (OER) catalyst is required to reduce the charge overpotential in the Li–O₂ system. Alternatively, via substitution of lithium by sodium, Hartmann et al. reported a rechargeable Na–O₂ battery with a very low charge overpotential of 0.2 V, even without any catalyst employed on the cathode support.³ Such low overpotential is mainly due to the relatively high conductivity of the discharge product, sodium superoxide (NaO₂). In contrast, the formation of LiO₂ in a Li–O₂ cell is very difficult because of its unfavorable thermodynamics.⁴ The formation of NaO₂ is accomplished in a one-electron transfer reaction:



From an energy density point of view, the one-electron transfer process (forming superoxide) has a theoretic specific energy (1108 Wh kg⁻¹) that is drastically lower than that of a cell with peroxide as discharge product via a two-electron process (1605 Wh kg⁻¹):⁵



With almost equal Gibbs free energy of formation shown in reactions 1 and 2, NaO₂ and Na₂O₂ are both thermodynamically possible discharge products in a Na–O₂ cell, with Na₂O₂ being slightly more favorable at standard conditions. In fact, sodium peroxide (mostly as hydrates) based Na–O₂ batteries have been reported. However, the results are ambiguous and the overpotentials are large (~1.6 V).^{6–8} Here, we have applied Pd nanoparticles as catalysts to promote the formation–decomposition of the sodium peroxide and substantially reduced the charge overpotential of such Na₂O₂ based cells to ~0.5 V.

The cell cathodes were fabricated by the atomic layer deposition (ALD) technique. ZnO was first deposited on the graphitized carbon black to passivate potential defect sites (denoted as ZnO/C).⁹ Pd nanoparticles were then grown on the ZnO-coated cathodes (denoted as Pd/ZnO/C). The average size of the Pd nanoparticles is around 5 nm (Figures 1a and S1), and the metallic character was confirmed by both the consistency to the diffraction peaks of palladium (ICSD 41517) by high-resolution X-ray diffraction (Figure 1b) and the characteristic *d*-spacing of Pd-(111) and atomic structure along Pd-[011] zone axis obtained from scanning transmission electron microscopy (STEM) (Figure 1a). X-ray absorption spectroscopy was applied to probe the chemical and coordination information. The XANES spectra at Zn K-edge (Figure S2a) indicate that the oxidation state of the Zn in the Pd/ZnO/C or the ZnO/C is ~2+, but the ZnO has lost its long-range order, forming amorphous phase (see detailed analysis in the SI). The XANES spectra at Pd K-edge (Figure S2b) show that the majority of the Pd is metallic, with a small amount on the surface being oxidized (Table S2). It is believed that such oxidized Pd may enhance the

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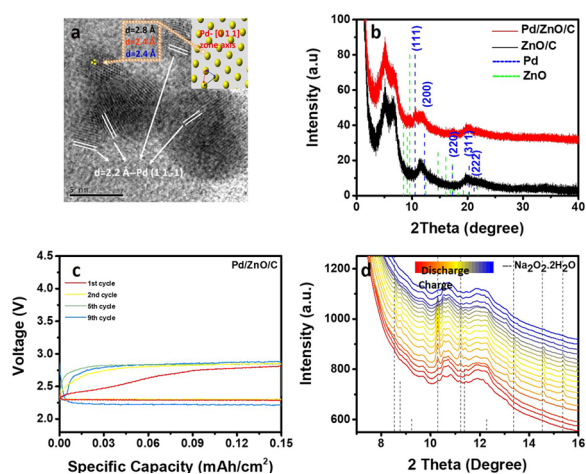


Figure 1. (a) Annular bright-field STEM image showing Pd-(111) lattice fringes (white arrows) and Pd-[011] zone axis atomic structure (yellow dots and the inset model) of Pd/ZnO/C sample. (b) HEXRD patterns of Pd/ZnO/C and ZnO/C samples (blue dashed line, Pd; green dashed line, ZnO). (c) Voltage profiles and (d) in situ XRD of Na–O₂ battery with Pd/ZnO/C as cathode.

catalytic activity of the Pd nanoparticles.¹⁰ The oxidation state of Pd is also influenced by its interaction with the ZnO layer, which was studied by extended X-ray absorption fine structure spectra. To avoid the influence of the oxygen, the Pd/ZnO/C sample was reduced by H₂ at 250 °C. As shown in Figure S3, due to the surface oxidation, the Pd–O peak at ~1.5 Å of Pd/ZnO/C cathode was much stronger than that of the Pd foil. However, after reduction, instead of being metallic, the intensity of the Pd–O peak of the Pd/ZnO/C was still noticeably higher, reflecting that the Pd formed a Pd–O bond with the oxygen in ZnO, which could not be reduced at this condition. The bond between Pd and ZnO allows the stable anchoring of Pd catalysts on the cathode and improves the battery cycle life, which was demonstrated by the improved cyclability (see the SI).

The catalytic effect of such Pd/ZnO/C cathode was examined in a Na–O₂ cell. Compared to the cell with a ZnO/C structured cathode (Figure S4a), a significant reduction of the charge overpotential (to ~0.5 V) was obtained with the Pd/ZnO/C cathode (Figure 1c), which validates the electrocatalytic role of the Pd nanoparticles. The high-energy X-ray diffraction (HEXRD) pattern under operando conditions was collected during the first cycle, which confirmed the formation–decomposition of Na₂O₂·2H₂O (Figure 1d). Raman spectra were used to investigate the surface of the discharge product Na₂O₂·2H₂O (Figure S5). Instead of the characteristic Raman peaks of Na₂O₂·2H₂O (ref 7), a peak at 1126 cm⁻¹ appeared, falling in the range of superoxide strength.⁴ The peak at 1502 cm⁻¹ is attributed to a strong interaction between superoxides and porous carbon surface.¹¹ Overall, the Raman spectra reflected the formation of an oxygen-rich superoxide-like product by the Pd nanoparticles, which is a plausible reason for the reduction of the charge overpotential.^{12–14}

The structural and morphological properties of the discharge product are also profoundly affected by the Pd/ZnO/C cathode because of the increasing active sites by the Pd nanoparticles. As shown in Figure S6a, after a 6 h discharge, featherlike structures formed on the cathode. The “feathers” became thinner (Figure S6b) and cracked into nanowires (Figure S6c) after 18 h, which developed a lot of holes and prevented the pores of the cathode from clogging. Such a highly porous framework allowed the

oxygen to access the inside of the cathode facilely. Meanwhile, more discharge product can be stored on the cathode. Consequently, the battery with Pd/ZnO/C cathodes exhibits an extremely large discharge capacity of 7.5 mAh/cm² (Figure S7). In contrast, the discharge product on ZnO/C merged together and formed a thicker layer on the cathode (Figure S6d–f). The pores of the cathode were blocked quickly by the discharge product, leading to the cell failure.

In summary, we have developed a cathode structure with Pd nanoparticles on the ZnO-passivated porous carbon to promote the formation–decomposition of Na₂O₂·2H₂O with porous structure under a two-electron electrochemical process in a Na–O₂ cell. The charge overpotential is reduced to ~0.5 V with a high capacity of 7.5 mAh/cm². This study demonstrates a new direction to achieve high-performance peroxide based Na–O₂ batteries through the rational design of electrode structures.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acseenergylett.7b01143.

Experimental methods and additional results (PDF)

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Notes

The authors declare no competing financial interest.

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