Electrocatalytic Iodine Reduction Reaction Enabled by Aqueous Zinc-Iodine Battery with Improved Power and Energy Densities

Longtao Ma*, Yiran Ying*, Shengmei Chen, Zhaodong Huang, Xinliang Li, Haitao Huang,* and Chunyi Zhi*

Abstract: Proposed are Prussian blue analogue hosts with ordered and continuous channels, and electrocatalytic functionality with open Co and Fe species, which facilitate maximum I2 utilization efficiency and direct I2 to I− conversion kinetics of the I2 reduction reaction, and free up 1/3 I− from I3−. Co[Co1/4Fe3/4(CN)6] exhibits a low energy barrier (0.47 kJ mol−1) and low Tafel slope (76.74 mV dec−1). Accordingly, the Co[Co1/4Fe3/4(CN)6]/I2//Zn battery delivers a capacity of 236.8 mAh g−1 at 0.1 A g−1 and a rate performance with 151.4 mAh g−1 achieved even at 20 A g−1. The battery delivers both high energy density and high-power density of 305.5 Wh kg−1 and 109.1 kW kg−1, higher than I2//Zn batteries reported to date. Furthermore, solid-state flexible batteries were constructed. A 100 mAh high capacity solid-state I2/Zn battery is demonstrated with excellent cycling performance of 81.2% capacity retained after 400 cycles.

Introduction

Anion-redox iodine-zinc (I2//Zn) is one of the most promising conversion battery chemistry based on iodine/iodide (I2/I−) redox couple in aqueous electrolytes. The I2/I− redox reaction ideally occurs at 0.62 V vs. standard hydrogen electrode (SHE) with two-electron (2 e−) transfer [Eq. (1)]. The I2/I− redox reaction is often depicted in two steps through the formation of I3− [Eq. (2) and (3)].

\[ \text{I}_2 + 2e^- \rightarrow 2I^- , \quad E^0 = 0.62 \text{ vs. SHE} \]  

\[ \text{I}_2 + 2/3e^- \rightarrow 2/3I_3^- \]

Metallic Zn shows fast redox chemistry based on Zn/Zn2+ redox couples in mild aqueous electrolyte. The Zn/Zn2+ redox reaction ideally occurs at −0.76 vs. SHE with 2e− transfer following the electrochemical equation:[2]

\[ \text{Zn} - 2e^- \rightarrow \text{Zn}^{2+}, \quad E^0 = -0.76 \text{ vs. SHE} \]

Based on the electrochemical characteristic of metallic Zn and I2, a I2//Zn battery is expected to provide a theoretical voltage of 1.38 V.

Up to now, most studies employ inactive carbon matrices as I2 hosts to utilize their excellent conductivity, porosity and high surface areas.[3] Despite these porous carbons can confine I2 within the cathodic chamber, the chaotic pore structure leads to inadequate utilization of I2 and slow ion diffusion. What’s more, because of electrochemically inactive properties of carbon-based frameworks, they fail to facilitate intrinsically sluggish reaction kinetics of I2 conversion. Moreover, in an electrocatalytically inactive host, the I2 reduction reactions (IRRs) occur following the Equation (2). This results in that only 2/3I2 contributes the usable capacity and the other 1/3I2 is utilized to form complexing agent of I3−. To sum up, these limitations of carbon host will lead to sluggish kinetics and limited I2 utilization, and thus, a poor rate capability and cycling stability of I2-based batteries.

A promising I2 host can be determined from the fast and complete transformation between initial I2 and final product of I−, and tightly anchor of both I2 and I− in cathode chamber. Prussian blue analogues (PBAs) possess an adequate porosity, and open transition-metal sites immobilized on functional organic ligands can effectively lower energy barrier of IRR, boost the conversion kinetics of I2/I−, and improve transform efficiency from I2 to I−. These properties may enable PBAs frameworks to significantly improve the electrochemical performance of I2//Zn batteries. However, the fundamental electrocatalytic kinetics of IRR are unexplored and the electrocatalytic effect is not adopted to address sluggish kinetics of the I2//Zn battery.
In this paper, we firstly use Co[Co\textsubscript{1–x}Fe\textsubscript{x}(CN)\textsubscript{6}] (0 ≤ x ≤ 1) as a host for I\textsubscript{2} to achieve a catalyzed IRR process to enhance the reaction kinetics and free-up all I\textsuperscript{−} without I\textsubscript{3} formed. Together with ordered pore structure, the fabricated electrodes deliver an unprecedentedly rate capacity and full utilization of I/I\textsubscript{3} redox. The Co[Co\textsubscript{1–x}Fe\textsubscript{x}(CN)\textsubscript{6}] exhibits lowest energy barrier (0.47 kJ mol\textsuperscript{-1}) and lowest Tafel slope (76.74 mV dec\textsuperscript{-1}) for IRR, suggesting the super-fast IRR kinetics of Co[Co\textsubscript{1–x}Fe\textsubscript{x}(CN)\textsubscript{6}]. The electrocatalytic activity originates from synergetic effects of Co and Fe open metal species. Accordingly, the Co[Co\textsubscript{1–x}Fe\textsubscript{x}(CN)\textsubscript{6}]/I\textsubscript{2}/Zn battery shows the best rate performance, with specific capacity of 150.1 mAh g\textsuperscript{-1} even at high current density of 200 mA g\textsuperscript{-1}. The maximum power density reaches to 22.3 kW kg\textsuperscript{-1} at high current density of 200 mA g\textsuperscript{-1}. Furthermore, the solid-state Co[Co\textsubscript{1–x}Fe\textsubscript{x}(CN)\textsubscript{6}]/I\textsubscript{2}/Zn battery could provide a high capacity of 229.6 mAh g\textsuperscript{-1} at 0.1 A g\textsuperscript{-1} and the capacity retains 150.1 mAh g\textsuperscript{-1} even at high current density of 4 A g\textsuperscript{-1}.

Results and Discussion

The PBAs are employed as I\textsubscript{2} host, owing to their high porosities, versatile functionalities with open metal species and controllable chemical composition. The intrinsically porous structure of PBAs enables a facile guests’ ions (such as I\textsubscript{2}, S\textsubscript{8}) infiltration and ion transportation, while the desirable component promises the incorporation of electroactive sites for various high-power battery systems (Figure 1a). The typical construction of PBA/I\textsubscript{2} is achieved in a two-step method, 1) synthesis and activation of PBAs, 2) impregnation of I\textsubscript{2} into PBA pores. PBA frameworks are synthesized by introducing sodium dodecyl sulfonate (SDS) as anionic surfactant to coordinate cobalt ions and then the coordination compounds combine with hexacyanoferrate and/or hexacyanocobaltate ions to form KCo[Co\textsubscript{1–x}Fe\textsubscript{x}(CN)\textsubscript{6}], KCo[Co(CN)\textsubscript{6}] and KCo[Fe(CN)\textsubscript{6}], respectively, at a controlled reaction rate. Then, Co[Co\textsubscript{1–x}Fe\textsubscript{x}(CN)\textsubscript{6}], Co[Co(CN)\textsubscript{6}] and Co[Fe(CN)\textsubscript{6}] frameworks are fabricated by electrochemically extracting K ions from KCo[Co\textsubscript{1–x}Fe\textsubscript{x}(CN)\textsubscript{6}], KCo[Co(CN)\textsubscript{6}] and KCo[Fe(CN)\textsubscript{6}], respectively.

Figure 1. a) Schematic illustration of the fabrication of I\textsubscript{2}-in-PBAs frameworks (denoted as PBAs/I\textsubscript{2}) and electrochemical procedure with electrocatalytically active sites of Co and Fe species. SEM image of b) Co[Co\textsubscript{1–x}Fe\textsubscript{x}(CN)\textsubscript{6}], c) Co[Co(CN)\textsubscript{6}], d) Co[Fe(CN)\textsubscript{6}], e) [Co\textsubscript{1–x}Fe\textsubscript{x}(CN)\textsubscript{6}]/I\textsubscript{2}, f) Co[Co(CN)\textsubscript{6}]/I\textsubscript{2}, and g) Co[Fe(CN)\textsubscript{6}]/I\textsubscript{2} frameworks.
The morphology and structure are investigated using scanning electron microscopy (SEM). SEM images of the Co[Co1/4Fe3/4(CN)6] and Co[Co(CN)6] reveal a truncated cube shape with sizes of ≈ 400 nm (Figure 1b,c). The truncated structure is related to the growth kinetics of PBAs frameworks at ripening procedure. The existence of hexacyanocobaltate ions give rise to the truncated cubic shape. While, the Co[Fe(CN)6] framework shows a well-define cube shape with a same size (Figure 1d). The regular morphology suggests the high crystallinity of our developed PBAs, in consistent with the XRD patterns (see Figure S1 in the Supporting Information).

The I2 molecules are successfully locked in PBA pores in a quantitative manner through melt diffusion at 80°C, as reflected in the drastic decrease in N2 uptakes of these PBA/I2 samples in comparison to the pristine PBAs (Figure S2). The original morphology of PBA frameworks is well preserved in this process, without any observable I2 species on the crystal surface (Figure 1e–g). The crystallinities of these PBAs are well-maintained as evidenced by the sharp peaks and systematic variation in the peak intensity of PBAs confirms the confinement of iodine species within PBA pores (Figure S3). The precise control of iodine content is conducted by varying the feeding ratio, and the exact loading amount is analyzed by thermogravimetric analysis (TGA; Figure S4). Given the high porosity of PBAs and strong chemical affinity (Figure S5), iodine in Co[Co1/4Fe3/4(CN)6] framework can reach to 61.2% by weight, higher than that of Co[Co(CN)6] (40.33%) and Co[Fe(CN)6] (31.21%) frameworks. We use ultraviolet-visible (UV-vis) measurement to assess the leaching of I2 from different electrodes by immersing Co[Co1/4Fe3/4(CN)6]/I2, Co[Co(CN)6]/I2, and porous carbon/I2 (for comparison) electrodes in 2 M ZnSO4 aqueous electrolyte. The results reveal that the confinement of I2 species in PBA frameworks by polar pore environment is significantly better than that of porous carbon. Meanwhile, the confinement of I2 species in Co[Co1/4Fe3/4(CN)6] framework is better than that of Co[Co(CN)6] and Co[Fe(CN)6] (Figure S6), which can be ascribed to that the synergetic effect of Fe and Co species can further improve the I2 adsorption.

Before the assembly of I2/Zn full cells, we systematically studied the electrocatalytic behavior of the PBAs for I2 reduction reaction (IRR). A series of electrochemical tests including cyclic voltammetry (CV) and A. C. impedance (EIS) are conducted in oxygen-free 2 M ZnSO4 with 5 mM I2 (Figures 2a–d). The results reveal a well-defined cycle shape with a same size (Figure 2a) and the electrocatalytic role of Co and/or Fe metal species in PBAs frameworks by polar pore environment is significantly better than that of porous carbon. Meanwhile, the confinement of I2 species in Co[Co1/4Fe3/4(CN)6] framework is better than that of Co[Co(CN)6] and Co[Fe(CN)6] (Figure S6), which can be ascribed to that the synergetic effect of Fe and Co species can further improve the I2 adsorption.

Remarkably, Co[Co1/4Fe3/4(CN)6] electrocatalyst shows the smallest η of 76.74 mV dec−1, compared with 117.22, 128.84 and 214. 35 mV dec−1 for Co[Co(CN)6], Co[Fe(CN)6] and porous carbon, respectively (Figure 2c).

To further study the origin of the improved electrocatalytic activity and kinetics of Co[Co1/4Fe3/4(CN)6] catalyzed IRR, the EIS spectra are conducted at reduction onset potential to evaluate the charge transfer resistance. Charge transfer is a key step for the transportation of ions and electrons to active centers to take part in IRR, which determines the electrocatalytic IRR kinetics. The Co[Co1/4Fe3/4(CN)6] electrocatalyst shows smallest charge transfer resistance of 11.4 ohm cm−2 during the IRR in comparison with Co[Co(CN)6] (24.1 ohm cm−2), Co[Fe(CN)6] (30.7 ohm cm−2) and porous carbon (42.5 ohm cm−2) (Figure 2d). Furthermore, the activation energy (Ea) that represents IRR barrier in this realm, is calculated using the Arrhenius equation:

\[ \frac{1}{R_a} = A \exp \left( -E_a / RT \right) \]  

Where, \( R_a \) is the charge transfer resistance, \( E_a \) is the activation energy. The \( E_a \) for Co[Co1/4Fe3/4(CN)6] electrocatalyst is 0.47 kJ mol−1, which is much smaller than Co[Co(CN)6] (1.27 kJ mol−1), Co[Fe(CN)6] (1.48 kJ mol−1) and porous carbon (1.92 kJ mol−1). The smallest \( E_a \) represent the superior kinetics of Co[Co1/4Fe3/4(CN)6] for electrocatalytic IRR.

We perform first-principles density-functional theory (DFT) calculations to elucidate the reaction spontaneity and the electrocatalytic role of Co and/or Fe metal species in PBA frameworks in IRR process and corresponding Gibbs free energy (ΔG) diagram is plotted in Figure 2e. Generally, low ΔG value reveals a high degree of spontaneity and the fast reaction rate. The fundamental IRR process for the catalysts involves a reduction reaction process from I2 molecules to intermediate product of I3−, to final product of I− ions.[3a] The latter reaction of I3− + 2e− → 3I− is the rate-determining step, corresponding to the largest ΔG value. As shown in Figure 2g, the transformations from I2 to I3− to I− are exothermic on all of three frameworks. The ΔG values for the potential-limiting step are 2.30, 2.47 and 2.17 eV for Co[Co(CN)6], Co[Fe(CN)6], and Co[Co1/4Fe3/4(CN)6] frameworks, respectively. It indicates the fastest kinetic conversion of I3− on the Co[Co1/4Fe3/4(CN)6] in electrochemical process, which is in consistent with above experimental results. It is noted that the reaction of I3− + 2e− → 3I− on the surface of graphene is endothermic and processed with high positive ΔG of 8.34 eV, indicating that this reaction is almost impossible to occur on the surface of graphene. Therefore, the PBAs framework with Fe and Co species can regulate the IRR kinetics with I2 formed on step ahead, while only common reaction pathway with I2 formed at the last step during IRR process on porous carbon. Consistently, experimentally, the distinct peak at 226 nm in UV-vis absorption spectra indexed to formed I− are detected in Co[Co(CN)6], Co[Fe(CN)6], and Co[Co1/4Fe3/4(CN)6] catalyzed IRR, while I2 at 288 nm and 354 nm is detected in porous carbon catalyzed IRR. It is significant that there almost no I3− formed in Co[Co1/4Fe3/4(CN)6] catalyzed
IRR, suggesting a complete conversion from I₂ to final product of I/C₂O₃.

As above characterization, I₂ has been successfully confined in Co[Co₁/₄Fe₃/₄(CN)₆], Co[Co(CN)₆] and Co[Fe(CN)₆] frameworks and they can catalyze I₂ conversion reaction. The propelled I₂/I/C₂O₃ conversion kinetics of three different frameworks in PBAs/I₂//Zn batteries are investigated by galvanostatic charge/discharge (GCD), CV and chronopotentiometry tests in 2 M ZnSO₄ aqueous electrolyte. The discharged capacity for Co[Co₁/₄Fe₃/₄(CN)₆]/I₂//Zn is 212.3 mAhg⁻¹ at current density of 0.2 Ag⁻¹, which are the highest among three electrodes. Interestingly, the Co[Co₁/₄Fe₃/₄(CN)₆]/I₂//Zn battery also exhibits the smallest electrochemical polarization (75.6 mV for Co[Co₁/₄Fe₃/₄(CN)₆]/I₂/Zn, 140.2 mV for Co[Fe(CN)₆]/I₂/Zn, as seen from the first charge/discharge process in Figure 3a, indicating the highest electrocatalytic ability and the fastest redox kinetics. The CV curves of batteries using above three different electrodes shown in Figure 3b displays one pair of redox peaks, which are ascribed to the I₂/I/C₂O₃ redox reaction. Figure 3c exhibits the onset potentials of three electrodes, derived from above CV curves. The Co[Co₁/₄Fe₃/₄(CN)₆]/I₂//Zn battery exhibits cathodic onset potential of 1.48 V, which is higher than those of the Co[Co(CN)₆]/I₂//Zn (1.45 V) and Co[Fe(CN)₆]/I₂//Zn (1.43 V). The anodic onset potential of the Co[Co₁/₄Fe₃/₄(CN)₆]/I₂//Zn battery is 1.23 V, lower than that of Co[Fe(CN)₆]/I₂//Zn (1.24 V) while higher than that of Co[Co(CN)₆]/I₂//Zn (1.22 V) batteries. Furthermore, the Co[Co₁/₄Fe₃/₄(CN)₆]/I₂//Zn battery shows highest cathodic and anodic peak potential of 1.26 V and 1.33 V, respectively (Figure 3d). On the other hand, the Co[Co₁/₄Fe₃/₄(CN)₆]/I₂//Zn battery has the lowest Tafel slope of 56.9 mV dec⁻¹ among

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**Figure 2.** a) CV curves of the Co[Co₁/₄Fe₃/₄(CN)₆], Co[Co(CN)₆], Co[Fe(CN)₆] and the referenced porous carbon electrocatalyst in nitrogen saturated 2 M ZnSO₄ + 5 mM I₂ solution using three-electrodes configuration, where the metallic Zn as reference and counter electrodes, glass carbon electrode deposited electrocatalyst as working electrode. b) The reduction potential and peak current density determined from CV curves. c) Corresponding Tafel plots from CV curves. d) EIS of Co[Co₁/₄Fe₃/₄(CN)₆], Co[Co(CN)₆], Co[Fe(CN)₆] and porous carbon in IRR. e) Corresponding Arrhenius curves exhibiting the linear relationship between logarithmic values of the reciprocal of charge transfer resistance and the reciprocal of absolute temperatures. f) Comparison of activation energies of Co[Co₁/₄Fe₃/₄(CN)₆], Co[Co(CN)₆], Co[Fe(CN)₆] and porous carbon in IRR at the onset potential. g) The Gibbs free-energy diagrams of I₂ reduction reaction on Co[Co(CN)₆], Co[Fe(CN)₆], Co[Co₁/₄Fe₃/₄(CN)₆] and bilayer graphene, where the * represent active site. h) UV-vis absorption spectra of electrolytes for Co[Co₁/₄Fe₃/₄(CN)₆], Co[Co(CN)₆], Co[Fe(CN)₆] and porous carbon after sufficient IRR.
the three electrodes (Figure 3e), which are also derived from CV curves. The above results suggest the fast electrocatalytic I2/I⁻ conversion of Co[Co 1/4Fe3/4(CN)6] framework and the remarkable enhancement of the redox kinetics of the I2/I⁻ couple by the synergetic effects of Fe and Co species.

Figure 3f illustrates the specific power delivered and the discharged voltage-current density (V–I) curves of the batteries, in which P values are calculated by the equation of 

\[ P = \frac{VI}{C} \]

Compared to Co[Co(CN)6]/I2//Zn and Co[Fe(CN)6]/I2//Zn battery, the Co[Co 1/4Fe3/4(CN)6]/I2//Zn battery shows a significantly lower voltage drop and encouragingly an ultrahigh power delivered (i.e. \( P_{\text{peak}} \) of 22.3 kW kg\(^{-1}\)), while that of Co[Co(CN)6]/I2//Zn and Co[Fe(CN)6]/I2//Zn batteries are 14.8 and 13.2 kW kg\(^{-1}\), respectively. This value far outperforms all of reported batteries, that is, NiS-coated Ni0.95Zn0.05(OH)2//Zn (18.8 kW kg\(^{-1}\)),\[6\] Co//Zn battery (12.6 kW kg\(^{-1}\)),\[7\] Ni//MH battery (4.8 kW kg\(^{-1}\));\[8\] MnO2//Zn battery (9.45 kW kg\(^{-1}\));\[9\] The high power delivered of the batteries originates from fast electrochemical reaction kinetics. Figure 3g presents the peak current density (\( i_p \)) of both the anodic and cathodic reactions versus the square roots of scan rates (\( n^{1/2} \)), derived from CV profiles of each electrochemically active species under different scan rates (Figure S7). Meanwhile, the b values obtained from the CV curves are 0.629 and 0.638 for Co[Co 1/4Fe3/4(CN)6]/I2/Zn, 0.726 and 0.672 for Co[Co(CN)6]/I2/Zn, 0.638 and 0.662 for Co[Fe(CN)6]/I2/Zn batteries, suggesting ion diffusion controlled battery behavior (Figure S8). The plots of \( i_p \) vs. \( n^{1/2} \) for three of Co[Co 1/4Fe3/4(CN)6]/I2, Co[Co(CN)6]/I2 and Co[Fe(CN)6]/I2 show a linear relationship, also suggesting that both reduction and oxidation reaction of I2 are controlled by mass transport.[10] The diffusion coefficient (D) can be calculated with the slope of these plots, according to the Randle-Sevcik equation.[11] The resulted diffusion coefficient values of Zn\(^{2+}\) ions are 3.64 × 10\(^{-6}\) cm\(^2\) s\(^{-1}\) for Co[Co 1/4Fe3/4(CN)6]/I2, much higher than that of 8.93 × 10\(^{-7}\) cm\(^2\) s\(^{-1}\) for Co[Co(CN)6]/I2 and 1.32 × 10\(^{-7}\) cm\(^2\) s\(^{-1}\) for Co[Fe(CN)6]/I2. The above results demonstrate that Zn\(^{2+}\) diffusion kinetics for the electrode is significantly enhanced by Co[Co 1/4Fe3/4(CN)6] framework.

The above results demonstrate the super-fast IRR kinetics and thermodynamically favorable conversion between I2 and I⁻ in the Co[Co 1/4Fe3/4(CN)6]/I2 framework. We further compare the rate performance of Co[Co 1/4Fe3/4(CN)6]/I2/Zn battery with inactive carbon/I2//Zn battery and other reported
I\(/\)Zn batteries. Figure 4a shows the rate capability of Co-[Co\(_{1/4}\)Fe\(_{3/4}\)(CN)\(_6\)]/I\(/\)Zn batteries at rates from 0.1 to 20 A g\(^{-1}\). At current density of 0.1 A g\(^{-1}\), the discharge capacity and plateau of Co-[Co\(_{1/4}\)Fe\(_{3/4}\)(CN)\(_6\)]/I\(/\)Zn (236.8 mAh g\(^{-1}\) with middle discharge voltage (\(E_{\text{mid,d}}\) of 1.27 V) are much higher than that of inactive carbon/I\(/\)Zn batteries (176.3 mAh g\(^{-1}\) with \(E_{\text{mid,d}}\) of 1.24 V) (Figure 4b). Specifically, the distinction is significantly amplified at high rates. The discharge capacity of Co-[Co\(_{1/4}\)Fe\(_{3/4}\)(CN)\(_6\)]/I\(/\)Zn battery retains 151.4 mAh g\(^{-1}\) (63.9\% initial capacity) at high rate of 20 A g\(^{-1}\), while only 23.7 mAh g\(^{-1}\) is maintained at only 5 A g\(^{-1}\) and I\(/\) conversion plateau disappears for carbon/I\(/\)Zn batteries. Meanwhile, excellent rate performance is much better than other PBA/I\(/\)metal batteries and all reported I\(/\)metal batteries including I\(/\)Zn, Fe, Al, Mg, Li batteries (Figure 4c, Figure S9). Moreover, the Co-[Co\(_{1/4}\)Fe\(_{3/4}\)(CN)\(_6\)]/I\(/\)Zn battery exhibits smaller voltage polarization at higher rates, with a smaller substantial voltage loss (\(E_{\text{mid,d}}\)) of 0.0492 V, much smaller than that of inactive carbon/I\(/\)Zn. The discharge plateau disappears when discharge current increases to 5 A g\(^{-1}\), suggesting no I\(/\) conversion reaction in carbon/I\(/\)Zn batteries at high rate due to sluggish I\(/\) conversion kinetics.

We plot the gravimetric energy density and power density of PBA/I\(/\)Zn batteries and other reported Zn batteries for comparison in Figure 4d. Both high energy density and high-power density (305.5 Wh kg\(^{-1}\) at 375.9 W kg\(^{-1}\) and 179.0 Wh kg\(^{-1}\) at 109.1 kW kg\(^{-1}\)) can be simultaneously achieved for Co-[Co\(_{1/4}\)Fe\(_{3/4}\)(CN)\(_6\)]/I\(/\)Zn battery based on cathode active materials. The electrochemical performances far outperform those of reported I\(/\)Zn batteries and even most aqueous Zn-ion batteries. The cyclic stability is another key factor for practical application of I\(/\)Zn batteries. The Co-[Co\(_{1/4}\)Fe\(_{3/4}\)(CN)\(_6\)]/I\(/\)Zn battery displays superior cycling performance, with a high capacity of 165.6 mAh g\(^{-1}\) retained (80.2\% capacity retention) even after 2000 cycles at 4 A g\(^{-1}\) at nearly 100\% coulombic efficiency (Figure 4e). In contrast, only 87.6 mAh g\(^{-1}\) after 1100 cycles and 43.3 mAh g\(^{-1}\) after 980 cycles are maintained for Co-[Co(CN)\(_6\)]/I\(/\)Zn and Co-[Fe(CN)\(_6\)]/I\(/\)Zn batteries, respectively. The excellent lifespan of Co-[Co\(_{1/4}\)Fe\(_{3/4}\)(CN)\(_6\)]/I\(/\)Zn battery originates from effectively electrochemical conversion of I\(/\) redox couple and great physiochemical confinement effects of Co-[Co\(_{1/4}\)Fe\(_{3/4}\)(CN)\(_6\)] framework for I\(/\) and ZnI\(_2\) without undesirable leakage (Figure S10).

We employ ex-situ XRD and X-ray photoelectron spectroscopy (XPS) to investigate the structure and surface chemistry changes of the Co-[Co\(_{1/4}\)Fe\(_{3/4}\)(CN)\(_6\)]/I\(/\)Zn cathode at different charge/discharge states. The peak at 17.3\° in XRD
The pattern shifts to high degree at fully discharged state and moves back to initial state at following charged state, suggesting the insertion of Zn\(^{2+}\) into Co\([\text{Co}_{1/4}\text{Fe}_{3/4}(\text{CN})_6]\) framework (Figure S11). The XPS high-resolution I 3d spectrum peaks located at 630.6 eV and 619.1 eV are indexed to I–O and I–C bond, respectively\(^{[12]}\) (Figure 4f). After a full discharge to 0.5 V, the two peaks shift to 629.9 eV and 618.5 eV, respectively, indicating the reduction of I\(^+\) to a lower oxidation state (I\(^0\) : Figure 4g). After following full charge to 1.6 V, these peaks move to original positions, indicating oxidation of I\(^+\) back to elemental I\(^0\) (Figure 4h). The XPS high-resolution Fe 2p (Figure S12a–c) and Co 2p (Figure S12d–f) spectra maintain almost unchanged at initial, fully discharged and following fully charged states, suggesting the nonparticipation of PBAs in redox reaction.

In light of high-performance Co\([\text{Co}_{1/4}\text{Fe}_{3/4}(\text{CN})_6]\)/I\(_2\)//Zn battery, we then construct solid-state battery using Co\([\text{Co}_{1/4}\text{Fe}_{3/4}(\text{CN})_6]\)/I\(_2\) as cathode, electro-deposited Zn as anode and polyacrylamide (PAM) hydrogel as electrolyte. The typical one pair of redox peaks in CV curves is indexed to reduction and oxidation of I\(_2\) during charge/discharge process (Figure 5a). Figure 5b, c shows galvanostatic charge/discharge profiles at different current densities from 0.1 to 4 A g\(^{-1}\) and rate performance, respectively. The solid-state Co\([\text{Co}_{1/4}\text{Fe}_{3/4}(\text{CN})_6]\)/I\(_2\)/Zn battery exhibits high capacity of 229.6 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\), with \(\bar{E}_{\text{mid},d}\) of 1.27 V (vs. Zn/Zn\(^{2+}\)). The capacity retains 150.1 mAh g\(^{-1}\) even at 4 A g\(^{-1}\), suggesting fast electrochemical kinetics of Co\([\text{Co}_{1/4}\text{Fe}_{3/4}(\text{CN})_6]\)/I\(_2\) and effective Zn\(^{2+}\) ion transport (0.12 S cm\(^{-1}\), Figure S13) of PAM hydrogel electrolyte. In addition, as shown in Figure 5d, the designed battery is capable of undergoing 1500 full charge/discharge cycles with 83.6% capacity retained at 2 A g\(^{-1}\) at nearly 100% coulombic efficiency. We then fabricate a high-energy (100 mAh) flexible solid-state battery in ambient air without any complicated procedures or protection. Remarkably, our Co\([\text{Co}_{1/4}\text{Fe}_{3/4}(\text{CN})_6]\)/I\(_2\)/Zn battery shows excellent cycling performance of 81.2% capacity retention after 400 cycles (Figure 5e).

As a result of its flexible components (carbon fiber cloth (CFC) collector, PAM hydrogel electrolyte), our solid-state Co\([\text{Co}_{1/4}\text{Fe}_{3/4}(\text{CN})_6]\)/I\(_2\)/Zn battery is expected to possess a high flexibility. As a demonstration of this superiority, the battery is fixed at bending angle of 180°, squeezing and rolling deformation, and the corresponding cycling performances at 0.5 A g\(^{-1}\) are shown in Figure 5f. The specific capacity of batteries maintained almost unchanged after continuous bending cycles at 180°, squeezing deformation and rolling deformation, indicating its excellent stability against deformations. Interestingly, our developed solid-state battery can be readily integrated into clothing fabrics like hat and T-shirt. We fabricated a tandem device with three individual batteries connected in series to provide a working voltage of 3.7 V and it is sewn onto hat and T-shirt. As shown in Figure 5g,h, the tandem device can power the commercial light-emitting diode.

**Figure 5.** a) CV curves of solid-state Co\([\text{Co}_{1/4}\text{Fe}_{3/4}(\text{CN})_6]\)/I\(_2\)/Zn batteries at scan rate of 0.2 mV s\(^{-1}\). b) Galvanostatic charge/discharge profiles of battery at different current densities. c) Rate performance. d) Cyclic stability at 2 A g\(^{-1}\). e) Cycling performance of 100 mAh high-capacity solid-state Co\([\text{Co}_{1/4}\text{Fe}_{3/4}(\text{CN})_6]\)/I\(_2\)/Zn battery. f) Cyclic stability of solid-state Co\([\text{Co}_{1/4}\text{Fe}_{3/4}(\text{CN})_6]\)/I\(_2\)/Zn battery at initial state and bending, squeezing, rolling deformations. Optical image of three batteries connected in series powering g) an LED with “CITYU” pattern integrated into a hat, and h) an electroluminescent panel integrated into a T-shirt.
(LED) with a “CITYU” pattern and electroluminescent panel, respectively.

**Conclusion**

The widely used porous carbon host for I$_2$ shows unordered pore structure and the electrochemically inactive property, limiting ion diffusions, I$^-$ ions utilization efficiency and electrochemical kinetics. PBAs with ordered 3D porous structure give full access to ion diffusion throughout the whole charge/discharge process. More importantly, the metallic Co and Fe species act as electrocatalytic sites to elevate electrochemical kinetics of IRR and free-up 1/3 unserviceable I$^-$ for energy storage. The Co[Co$_{1/4}$Fe$_{3/4}$(CN)$_6$] exhibits lowest activation energy barrier of 0.47 kJ mol$^{-1}$ and smallest Tafel slope of 76.74 mV dec$^{-1}$ for IRR from I$_2$ directly to I$^-$. Correspondingly, the Co[Co$_{1/4}$Fe$_{3/4}$(CN)$_6$]/I$_2$/Zn battery exhibits high capacity of 236.8 mAh g$^{-1}$ and high power density of 109.1 kW kg$^{-1}$. Furthermore, we construct solid-state Co[Co$_{1/4}$Fe$_{3/4}$(CN)$_6$]/I$_2$/Zn battery, which shows high capacity of 229.6 mAh g$^{-1}$ at 0.1 A g$^{-1}$ and good flexibility. The electrochemical performance maintains unchanged under bending, squeezing and rolling deformations. Meanwhile, the battery can be easily sewed into clothing fabrics to power electronics.

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** batteries · electrochemistry · iodine · reduction · zinc

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Electrocatalytic Iodine Reduction Reaction Enabled by Aqueous Zinc-Iodine Battery with Improved Power and Energy Densities

A Prussian blue analogue host with ordered and continuous channels, and electrocatalytic functionality, facilitates maximum I$_2$ utilization efficiency and direct I$_2$ to I$^-$ conversion kinetics of the I$_2$ reduction reaction, and frees up 1/3 I$^-$ from I$_3$$^-$. The Co[Co$_{1/4}$Fe$_{3/4}$(CN)$_6$]/I$_2$//Zn battery delivers a capacity of 236.8 mAh g$^{-1}$ at 0.1 A g$^{-1}$, rate performance with 151.4 mAh g$^{-1}$ achieved even at 20 A g$^{-1}$, and high-energy and high-power density (305.5 Wh kg$^{-1}$ and 109.1 kW kg$^{-1}$).