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Three-Dimensional Fibrous Iron as Anode Current Collector for Rechargeable Zinc–Air Batteries

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Abstract: A three-dimensional (3D) fibrous structure with a high active surface and conductive pathway proved to be an excellent anode current collector for rechargeable zinc–air batteries (ZABs). Herein, a cost-effective and highly stable zinc (Zn) electrode, based on Zn electrodeposited on iron fibers (Zn/IF), is duly examined. Electrochemical characteristics of the proposed electrode are seen to compete with a conventional zinc/nickel foam (Zn/NF) electrode, implying that it can be a suitable alternative for use in ZABs. Results show that the Zn/IF electrode exhibits an almost similar trend as Zn/NF in cyclic voltammetry (CV). Moreover, by using a Zn/IF electrode, electrochemical impedance spectroscopy (EIS) demonstrates lower charge transfer resistance. In the application of a rechargeable ZAB, the fibrous Zn/IF electrode exhibits a high coulombic efficiency (CE) of 78%, close to the conventional Zn/NF (80%), with almost similar capacity and lower charge transfer resistance, after 200 charge/discharge cycles. It is evident that all the positive features of Zn/IF, especially its low cost, shows that it can be a valuable anode for ZABs.

Keywords: zinc–air battery; porous zinc anode; iron fibers; electrochemical performances

1. Introduction

A cost-effective, reliable and affordable electrical energy storage system (EESS) with low environmental impact is necessary for renewable energy generation and conversion [1]. In both supply and demand, EESS plays a vital role in enhancing the stability and flexibility of a power grid [2,3]. The most common kind of EESS is a rechargeable battery. Lithium-ion batteries (LIBs) are widely recognized as the most viable solution due to their excellent performance and flexible applications. Nevertheless, LIBs exhibit numerous deficiencies, such as high cost and safety issues [4–6]. Specifically, there are concerns regarding raw material supply [7,8].

Unlike lithium (Li), Zn is more cost-effective (~\$0.9/lb) and globally abundant (~300 times higher than Li in the earth's crust) [9,10]. A Zn anode offers greater safety and a higher specific volumetric capacity (5855 mAh/cm³) compared to that of Li (2066 mAh/cm³) [11,12]. Furthermore, Zn is primarily used in industry and can be easily recycled using existing technologies [13]. Zn is also considered a significant contributor to the circular economy.

Zinc–air batteries (ZABs) are particularly attractive as a sustainable and inexpensive solution for large-scale EESS, owing to their low cost, eco-friendliness, safety, long-term durability and very high energy density (1.35 kWh/kg) [14,15]. Primary ZABs have been most successfully implemented in medical and telecommunication applications, such as hearing aids, navigation lights and railway signals. ZABs consist of three major parts: a Zn anode, an electrolyte and an air cathode. In the preparation of air cathodes, catalytic layers are usually used either in single layer or multiple layer. This is carried out in order to enhance the slow kinetics of the oxygen reduction reaction (ORR) and to improve the cycle life of the ZABs. Some instances of commonly used catalysts in ZAB cathodes are silver [14,15] and manganese dioxide (MnO_2). Furthermore, in ZABs, the electrolyte plays a crucial role as a medium for ionic migration during discharge/charge. Aqueous alkaline solutions, such as the potassium hydroxide (KOH) solution, have high ionic conductivity and relatively high influence on ORR; therefore, they are considered suitable for use in ZABs. Furthermore, inorganic additives, salts and organic solvents are sometimes added to the KOH electrolyte to suppress the problems of dendrite growth and Zn corrosion as the result of the hydrogen evolution reaction (HER) in ZABs. A unique feature of ZABs is that only the active anode material (Zn) is stored inside the battery system. In contrast, the active cathode material (oxygen) is drawn directly from the ambient air. Considering all positive features of ZABs, there are some challenges that have to be taken into account, such as dendrite growth, shape change as well as passivation of the Zn anode upon cycling [16]. The adoption of a proper anode structure can overcome these common challenges and can enhance the performance of ZABs [17].

The aforementioned issues can be solved by adopting a three-dimensional (3D) porous structure of the Zn anode [18]. Thereby, the current is uniformly distributed throughout the electrode, while the void structure constrains the dissolution/precipitation processes. Typically, in ZABs, the use of porous anodes is advantageous in presenting a large active surface for the deposition of Zn ions, indicating a great specific capacity for energy storage purposes [19]. Traditionally, nickel foam (NF) has been widely used as the anode current collector as it offers a large active surface and a continuous conductive porous 3D network. NF, despite its high porosity and surface area, has good electrical conductivity, high corrosion resistance and superior mechanical properties, and also has been found to be an excellent electrocatalyst for HER [20,21]. The usage of nickel is linked to economic development; the world's demand for nickel has increased at an annual rate of 3.8% since 2000. Furthermore, nickel is only mined in a small selection of countries, e.g., Indonesia, Philippines and Russia, which creates a potential supply risk [22]. Thus, the development of alternative, inexpensive earth-abundant electrode materials with improved or comparable electrochemical properties to NF and a high active surface is of great significance. A higher surface area of anode material offers several benefits. It provides smaller local current densities and suppresses the potential of passivation of the Zn anode. Likewise, it reduces the featured dendrite growth [23]. Iron fibers (IF) are highly porous renewable materials which are cheap and have high conductivity due to mechanical integrity and connectivity of the fibrous structure. Therefore, they are considered a promising candidate for this purpose [24].

Synthesis and application of porous anode material have continuously been a focal point among many researchers [25]. Previously, performance of a Zn anode was enhanced using fibrous materials for a high power application of ZABs; large capacity at a high discharging current was reported [26]. In order to inhibit the passivation of the Zn anode induced by pore plugging, a pasted Zn electrode was prepared from an aqueous slurry containing Zn oxide (ZnO), polytetrafluoroethylene (PTFE), lead oxide (PbO) (to suppress hydrogen evolution) and cellulose. According to the results, both cycle life and peak power drain capability were improved by the addition 10 wt.% cellulose to the pasted Zn electrode [27]. Moreover, a porous Zn anode made from Zn powder, rather than a planar Zn plate, was demonstrated. The impact of a higher effective surface area on anode mass utilization and capability of the rechargeable alkaline battery was investigated. As a result, a larger discharge capacity was observed for the porous Zn electrode than that of the planar Zn plate [28].

This work presents a low-cost alternative to the conventional NF to support the anode material. The main aim is to further reduce the cost of ZABs. Hence, a 3D fibrous material as anode current collector was synthesized from IF. Initially, it was intended to create a consistent IF platform to support Zn on the anode current collector effectively. Then, the prepared IF-based anode electrode underwent a series of analyses to determine its electrochemical properties. Furthermore, the synthesized Zn/IF anode was implemented and examined in a ZAB. Consequently, the performance of the featured electrode was investigated and compared with a conventional Zn/NF electrode.

2. Materials and Methods

2.1. Chemicals and Materials

An NF sheet of 99.97% purity, 100 pores per inch and 1 mm thickness (Qijing Trading Co., Ltd., Jiangxi, China) was used as current collector for the anode (in fabrication of benchmark electrode) and cathode (in ZAB). An IF of 99% purity, 20 μm thickness and 1.8 nm pore size (Ezhou Baofeng Metal Wool Technology Co., Ltd., Hubei, China) were used as the anode current collector and working electrode for Cyclic Voltammetry (CV) analysis. Zn foil of 99.9% purity, (Shandong AME Energy Co., Ltd., Shenzhen, China) and Zn (Sigma-Aldrich, USA) were used in the electroplating process. A copper sheet of 150 μm thickness (Yueqing Kangsheng Copper Co., Ltd., Zhejiang, China) was used as anode current collector (for Zn/IF electrode). Potassium hydroxide (KOH) pellets of 99% purity (Elago Enterprises Pty. Ltd., Sydney, Australia) and zinc oxide (ZnO) grade AR (Elago Enterprises Pty. Ltd., Sydney, Australia) were used in the synthesis of the electrolyte. Manganese (IV) oxide (MnO_2), 5 μm , 99.99% purity (Sigma-Aldrich, USA), with carbon blacks (XC 72R), (Cabot Corporation, United States) and carbon blacks (BP2000) (Cabot Corporation, United States) were used in the preparation of the cathode electrode. Finally, polyvinylidene fluoride (PVDF), (Sigma-Aldrich, USA), graphite (Timcal KS6), (Sigma-Aldrich, USA) and dimethyl fumarate (DMF), (Sigma-Aldrich, USA) were used in the preparation of the binder.

2.2. Electrode and Battery Fabrication

As shown in Figure 1, a ZAB was assembled and used to evaluate polarization and galvanostatic discharge characteristics. The battery consisted of a Zn/IF electrode as an anode, a porous air cathode electrode, a cylindrical cell casing and a solution electrolyte. To fabricate the anode electrode, copper sheets were cut in pieces of $5 \times 1 \text{ cm}^2$ in dimension. Then, the sheets were smoothed with sandpaper (No. 4) and washed with acetone. Initially, the IF were washed with acetone and heated in an incubator for 4 h at $T = 60^\circ\text{C}$. Next, the IF were cut to cover an area of copper ($1 \times 1 \text{ cm}^2$) at a density of 40 mg/cm^2 . The IF were adhered to a copper sheet using a binder comprised of a graphite and PVDF mixture with a ratio of 85:15 (wt./wt.) dissolved in 5 mL dimethyl fumarate (DMF) solvent. As illustrated in Figure 2, the surface of the copper was intended to be fully covered by the IF to avoid the contact of copper with the electrolyte solution. The electrode was placed into a vacuum cabinet at $T = 60^\circ\text{C}$. Finally, in preparation of the anode, a Zn was electroplated on the IF electrode using a Zn sulfate solution (1 M) under a current density of 20 mA/cm^2 , for a duration of 1 h.

The porous air cathode consisted of three layers: a gas diffusion layer, a current collector and a catalyst layer. The MnO_2 -based catalyst layer, which is directed to be in contact with the electrolyte, was synthesized via mixing powdered carbon (BP2000) and MnO_2 in a ratio of 70:30 (wt./wt.). Polystyrene was added as binder along with toluene 5%. Then, this mixture was applied to the inner surface of the NF (current collector) via brushing and inserted into a hot press for 10 min at $T = 150^\circ\text{C}$ [29]. The air side (gas diffusion layer) consisted of combined carbon (XC 72R) and polytetrafluoroethylene in a ratio of 40:60 (wt./wt.). Next, 35 mL ethanol was added as solvent, applied onto the outer side of the NF and hot pressed at $T = 350^\circ\text{C}$ for 15 min. Furthermore, an aqueous solution containing 6 M (KOH) and 0.24 M (ZnO) having a total volume of 20 mL was used as electrolyte solution.

Figure 1. Schematic demonstration of the zinc–air battery (ZAB).

Figure 2. The anode electrode consisted of iron fibers (IF) adhered to the copper sheet.

2.3. Characterization and Measurement

For the purpose of electrochemical characterization, an electrochemical cell, having three electrodes, was employed accordingly. Electrochemical characterization techniques involved the following: CV, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (Tafel experiment) and chronoamperometry. Further, morphology of the Zn deposition, on both anodes, was studied via scanning electron microscopy (SEM), using a field emission SEM (ZEISS Sigma 500, Carl Zeiss AG, Oberkochen, Germany), at an accelerating voltage between 5 kV at a working distance between 1 and 5 mm. Energy dispersive X-ray (EDX) spectroscopy (SmartEDX, Carl Zeiss AG, Oberkochen, Germany) by a 30 mm² detector using holey carbon grids was undertaken for elemental mapping. The Brunauer–Emmett–Teller (BET) analysis was conducted via the 3Flex physisorption setup (ASAP2010, Micromeritics Instrument Corp, Ottawa, Ontario, Canada) using nitrogen at 77 K to determine the surface area of the samples. The samples were outgassed via the use of nitrogen at 150 °C for 16 h before measurements. For all electrochemical characterizations, a Zn anode was used as working electrode, a platinum plate as counter electrode and mercury/mercury oxide (Hg/HgO) as reference electrode; except for multicycle CV where the working and counter electrodes were used in reverse order. Electrochemical techniques were carried out via a potentiostat/galvanostat with

an impedance measurement unit (PAR VersaSTAT 3A, AMETEK Inc., Berwyn, Pennsylvania, USA), and the data were obtained and analyzed using VersaStudio software (2.60.6, AMETEK Inc., Berwyn, Pennsylvania, USA). CV was performed in the range of -1.6 to -0.7 V vs. Hg/HgO at a scan rate of 7 mV/s. For potentiodynamic polarization, the measurements were carried out as follows: anode materials were immersed for 30 min in solution electrolyte, at room temperature, within the voltage range of -0.5 to $+0.5$ V vs. open-circuit voltage (OCV) at a scan rate of 1.67 mV/s. EIS was applied at a frequency range of 100 kHz to 0.1 Hz at 10 mV of amplitude. Thus, the obtained EIS spectra were analyzed via Zsimpwin software (3.60, AMETEK Inc., Berwyn, Pennsylvania, USA). The influence of Zn-deposition by an applied potential was investigated via chronoamperometry in a range of -1.45 to -1.60 V vs. Hg/HgO. Furthermore, the electrostatic charge/discharge performance of the Zn electrodes was evaluated for cyclic stability and cycle lifespan, using a ZAB wherein the cell was charging with a constant current of 10 mA for 160 s followed by resting for 60 s, and then discharging under a constant current density of 10 mA/cm² to a cut-off voltage of 0.8 V. Polarization characteristics of the ZAB were evaluated by a battery testing system (NEWARE, CT-4008-5V20mA, Neware Technology Ltd., Shenzhen, China). The data were collected and analyzed via battery tester software (BTS 7.6.0, Neware Technology Ltd., Shenzhen, China).

3. Results and Discussion

3.1. Electrochemical Characterization

CV was performed on three substrates: a pure copper sheet, a copper plate having IF adhered to IF/Cu and NF. This was carried out in order to examine whether the substrates, to some extent, were involved with the redox chemistry that occurred at the electrode/electrolyte interface. As shown in Figure 3, CV was performed at a scan rate of 7 mV/s within a potential range of -1.7 to 0.5 V vs. Hg/HgO.

Figure 3. Cyclic voltammetry (CV) of copper sheet, IF/Cu and NF substrates at a scan rate of 7 mV/s within a potential range of -1.7 to 0.5 V vs. Hg/HgO.

For copper and NF substrates, the voltammograms exhibited a smooth-lined shape with no substantial peaks, indicating the lack of any oxidation/reduction reactions. However, some small peaks were observed between the potentials of -0.889 and -0.683 V vs. Hg/HgO in the voltammogram of the IF/Cu substrate. The magnitude of the peaks is relatively small ($< \pm 5$ mA/cm²) and would most probably be eliminated when the IF surface has been fully coated by the Zn particles. The peaks were

in accordance with slight oxidation of iron into Fe^{2+} and Fe^{3+} ions while reacting with the hydroxide ions from the electrolyte, according to Equations (1)–(3) [30]:

Due to the high active area/porosity introduced by the IF, when the Zn/IF electrode is in contact with an electrolyte, a higher number of metal ions can be dissolved from the anode surface into the solution medium and become involved in zincate formation reactions, according to Equation (4) and Equation (5). Thus, higher activity is expected to be attained in the presence of a porous anode.

To evaluate this, CV was adopted to investigate the electrochemical properties of the Zn/IF and Zn/NF anodes. Current density values were recorded when different potentials were applied to the system in the forward/reverse scan. In Figure 4a, the results of CV are shown. The voltammograms are almost similar for both anodes. However, there was not much difference in anodic/cathodic peaks, suggesting that an almost similar mechanism of Zn dissolution/deposition occurred in both electrodes. However, around the potentials of -1.15 to -1 V vs Hg/HgO a slightly larger magnitude of current density at the anodic peak was observed for the Zn/IF (351 mA/cm^2) rather than that of Zn/NF (347 mA/cm^2). Although the difference was not significant, the higher current density suggested that enhanced kinetics of oxidation and formation of zincate ions occurred in the forward scan, due to the presence of an electron transport channel throughout the porous region [31]. Moreover, a second anodic peak was observed for both electrodes in a reverse scan around the similar potential of the anodic peak. The formation of ZnO, on the forward scan, was followed by its precipitation on the electrode surface, thus forming a passive layer which reduced the active area of the electrode. However, the Zn ions which did not oxidize in the forward scan tended to oxidize in the reverse scan, due to the breakdown of the passive layer at the very oxidation potential range [32]. The Zn/IF electrode exhibited a smaller oxidation peak in reverse scan that slightly shifted to negative potentials, suggesting that the passivation film was more stable and less soluble in the presence of the fibrous iron electrode. As for the CV results, both electrodes exhibited the crossover between the anodic and cathodic traces at the potentials of 0.148 and 0.214 V vs. Hg/HgO—related to Zn/NF and Zn/IF, respectively. The crossover occurred due to the difference in deposition and dissolution onset potentials corresponding to nuclei formation on the electrode.

Figure 4b shows Nyquist diagrams of the Zn/IF and Zn/NF electrodes, at a frequency range from 100 kHz to 0.1 Hz with alternate current amplitude of 10 mV around OCV. In Supplementary Materials (Figure S1a,b), Bode diagrams are presented. In both cases, the spectrums have quite similar shapes, indicating the equivalent mechanism of Zn dissolution. Further, according to Figure 4b, the semicircles pertain to the charge-transfer resistance (R_{ct}), demonstrating the occurrence of charge transfer at the electrode/electrolyte interface. According to the EIS diagrams, Zn/IF exhibited a smaller semicircle at high frequency, thus denoting a lower charge transfer resistance and faster surface reactions than Zn/NF, which is considered an advantage in the charge/discharge processes. The smaller R_{ct} can be ascribed to the higher rate of anodic reactions and Zn dissolution indicated by the Zn/IF electrode [33]. An efficient electron transport for oxidation reaction is also attributed by the small charge transfer resistance. Moreover, no Warburg impedance was observed at a low frequency. Warburg impedance is associated with diffusion of soluble Zn ions from the electrode surface into the bulk electrolyte and is usually identified by a small inclined line at low frequencies [34,35]. EIS data including the R_{ct}

and solution resistance (R_s) were calculated from the equivalent circuit model to fit with the Nyquist plots. In Table 1, the results are shown. Q is a constant phase element describing the capacitance of the electrode/solution interface. R_s denotes the resistance between the reference and working electrodes, which depends on the type of ions, ionic concentration, ion conductivity, temperature, and other physicochemical characteristics of the solution electrolyte employed. In the EIS analysis, a similar electrolyte was used for both electrodes; thus, the R_s values were found to be close. Moreover, results confirmed the smaller charge transfer resistance of the Zn/IF electrode (4.877 Ω), which was about 0.47 percent lower than that of Zn/NF (9.215 Ω). Typically, the high electroactive area introduced by porous electrodes accommodates the strain induced by the volume variations during the deposition of Zn ions and therefore are capable of reducing the deterioration of the electrode surface, as compared to less porous types [36].

Figure 4. (a) CV at a scan rate of 7 mV/s within a potential range of −1.70 to −0.7 mV vs. Hg/HgO and (b) Nyquist plots with fitted lines and equivalent circuit model at a starting frequency of 100 kHz to 0.1 Hz for Zn/IF and Zn/NF around open-circuit voltage (OCV).

Table 1. Resistance values of Zn anodes in the solution electrolyte.

Anode	$R_S (\Omega)$	$R_{CT} (\Omega)$	$Q, CPE (S/s^n)$	
			$Y_0 (s^n/\Omega \times 10^6)$	$0 < n < 1$
Zn/IF	1.832	4.877	1.143×10^{-3}	0.845
Zn/NF	1.761	9.215	5.329×10^{-4}	0.905

The 3D structure of the anode surface corresponds with an altered corrosion inhibition property of the electrode. It is also crucial to determine the corrosion behavior of an electrode through understanding the kinetics of dissolution and hydrogen evaluation, as it significantly affects the performance and shelf-life of the batteries. Therefore, the potentiodynamic polarization analysis of the electrodes was carried out at a scan rate of 1.67 mV/s within the potential range of -0.5 to $+0.5$ V vs. OCV. In Figure 4, the results of the Tafel polarization analysis are indicated. In Table 2, the corrosion potential (E_{corr}) and corrosion current density (I_{corr}) and other parameters are listed.

Table 2. Corrosion parameters of metals in solution electrolyte.

Anode	E_{corr} (V vs. Hg/HgO)	I_{corr} (mA/cm ²)	α_a (mV/decade)	$-\alpha_c$ (mV/decade)	$R_p (\Omega)$	CR
Zinc Plate	−1.427	3.430	0.069	0.252	0.690	6.245
Zn/NF	−1.577	5.091	0.086	0.733	0.656	7.430
Zn/IF	−1.291	5.912	0.077	0.182	0.397	9.761

Following the Butler–Volmer equation (compact form) for the anodic and cathodic reactions, the Tafel equation can be described, as shown in Equation (6):

$$E - E_{corr} = \frac{2.3RT}{\alpha F} \log(i) - \frac{2.3RT}{\alpha F} \log(i_0) \quad (6)$$

where I and I_{corr} are the measured and corrosion current densities, respectively; E and E_{corr} are the electrode and corrosion potentials, respectively; and α is the symmetry factor. Tafel curves can be considered straight lines at potentials close to E_{corr} . The value of I_{corr} can be determined by the extrapolation of the cathodic Tafel curve to the E_{corr} . The slope of each Tafel curve represents the corresponding polarization resistance (R_p), which denotes the transition resistance between the electrodes and the electrolyte and is derived according to the well-known Stern–Geary equation [37], as shown in Equation (7):

$$R_p = \frac{\alpha_a |\alpha_c|}{2.303 I_{corr} (\alpha_a + |\alpha_c|)} \quad (7)$$

where α_a and α_c are the slopes of Tafel curves related to the anodic and cathodic branches of partial reactions, respectively. The corrosion rate (CR) generally corresponds to the corrosion current density along with the surface area of the working electrode (Zn) and alters due to porosity and accumulation of corrosion products [38]. CR can be determined by applying the parameters calculated, as in Equations (6) and (7), into the Faraday equation for linear polarization resistance, as shown accordingly in Equation (8):

$$CR = \frac{0.13 I_{corr} W_{eq}}{d} \quad (8)$$

where W_{eq} is the equivalent weight and d is the density of the sample electrode, respectively.

For a clearer understanding regarding the influence of different substrates on the corrosion of the Zn anode, the potentiodynamic polarization of the Zn/IF and Zn/NF electrodes has been compared with the pure Zn plate anode. As revealed in Figure 5a, the corrosion potential of Zn shifted negatively through the use of Zn/NF but positively through the use of Zn/IF. This suggests that the Zn/IF electrode further affected the anodic process of Zn corrosion in the electrolyte whereas Zn/NF mainly affected

the cathodic process. The lower corrosion potential via the use of NF corresponded with the more negative potential of hydrogen evolution, indicating that Zn/NF can enhance the charge efficiency if used in Zn-based batteries [39]. Moreover, the positive shift of E_{corr} associated with the Zn/IF electrode indicated that IF reduced the rates of the anode reactions. Thereby, it was seen to be effective in decreasing the corrosion susceptibility of the Zn anode. However, for both the Zn/IF and Zn/NF electrodes, cathodic and anodic branches shifted to higher current densities compared to the Zn plate while the shift was even bigger for the IF electrode. This suggested a higher rate of hydrogen evaluation and Zn dissolution associated with the use of porous electrodes. In Table 2, the polarization results are indicated, and the corrosion rate was calculated for each anode, accordingly. Higher corrosion current densities of 5.091 mA/cm² and 5.912 mA/cm² were attained for Zn/NF and Zn/IF, respectively, as compared to the I_{corr} of Zn plate (3.430 mA/cm²). The higher corrosion rates are indicators of lower polarization resistance, i.e., a lower corrosion inhibition property. Furthermore, both Zn/IF and Zn/NF electrodes exhibited a lower anodic slope of the Tafel curve than that of the Zn plate. The smaller slope indicated higher corrosion of the anode caused by higher kinetics of Zn dissolution in the electrolyte. In other words, corrosion on the Zn surface occurred due to the formation of a ZnO layer around the anode surface, which acted as a passivation layer and suppressed the dissolution of Zn ions in the electrolyte that eventually lowered the current density of the electrode. In addition, the hydrogen evolution in the cathodic branch of the Zn/IF electrode was observed to be more intensive as compared with the Zn plate and Zn/NF, whereby the former agreed with the results of CV, as shown in Figure 4a.

Figure 5. (a) Potentiodynamic polarization (Tafel) curves of the pure Zn plate, Zn/IF and Zn/NF anodes, at a scan rate of 1.67 mV/s. (b) Chronoamperometry of the Zn/IF electrode within a potential range of −1.45 to −1.60 V vs. Hg/HgO in an electrolyte solution.

In Figure 5b, the results of the chronoamperometry tests are shown. The Zn/IF electrode was used to determine the Zn deposition influenced by an applied potential. At each selected potential, the current-time transient for 30 min was observed. In higher potentials, noisy curves appeared due to the non-homogeneous distribution of deposits on the surface of the electrode, as a result of HER [40]. Potentials were selected in the range of −1.45 to −1.60 V vs. Hg/HgO associated with the cathodic region, whereby the highest rate of deposition/dissolution close to the surface of the electrode was observed (see Figure 4a). Results revealed that the reduction of Zn had decreased at potentials below −1.45 V vs. Hg/HgO. Moreover, the rising portion, which appeared at 0.025 min, was due to the Zn nucleation process [41]. In more negative potentials, particularly at −1.55 V vs. Hg/HgO, the current-time transition curve was non-smooth with currents being unstable. This was probably because of the smaller surface area and thus less conductivity of the electrode caused by the formation of hydrogen gas. This also suggests that more powerful reactions between the reduced electrode surface and hydrogen gas had taken place, which affected surface conductivity. Since water is a better

electron recipient than zincate ion, introducing more energy to the process will cause the hydrogen from hydrolyzed water (H^+) to take over the reaction with the released electron and to form H_2 . As a result, more HER occurred accordingly, as in Equations (9)–(11):

To further conceptualize the charge transfer, the CV plots for both the Zn/IF and Zn/NF anodes were obtained at various scan rates (5 to 20) mV/s in the electrolyte (Figure 6a,b). It is observed that when scan rates increased, the anodic peak currents linearly increased. However, the cathodic peaks are less dependent on the scan rate. Anodic peaks can be split into three distinct regions: charge transfer region, diffusion-controlled region and mixed charge transfer diffusion-controlled region. Typically, when current density changes linearly with the square root of the scan rate for the reduction process, this indicates that the peak is caused by ion diffusion. The effect of scan rate on the peak current i_c for simple redox reactions can be described by the Randles–Sevcik equation, as shown in Equation (12):

$$i_c = (2.99 \times 10^5) A \alpha^{0.5} v^{0.5} D_0^{0.5} C_0 \quad (12)$$

where i_c is the peak current density (mA/cm^2), α is the electron transfer coefficient, D_0 is the diffusion coefficient (cm^2/s), C_0 is concentration (mol/cm^3), A is the surface area (cm^2) and v is the scan rate (mV/s). The fitted lines for the logarithmic values of anodic peaks, as a function of root square of scan rates, were plotted (Figure 6b,c); the corresponding equations were derived accordingly, as shown in Equations (13) and (14):

$$\log(i_c) = 0.1085 \log v^{0.5} + 2.492 \text{ (for Zn/IF electrode)} \quad (13)$$

$$\log(i_c) = 0.0261 \log v^{0.5} + 2.476 \text{ (for Zn/NF electrode)} \quad (14)$$

Thus, the straight lines revealed slopes of 0.1085 and 0.0261 for Zn/IF and Zn/NF, respectively, which are lower than the theoretical value of 0.5 for a fully diffusion-controlled process.

As shown in Figures 7 and 8, the micrographs (200 $\times$) for Zn deposition on the active surface of IF and NF, after a 30 min duration, were studied at different potentials via SEM. As observed in Figure 7, from -1.60 V vs Hg/HgO (at $-180.90 \text{ mA}/\text{cm}^2$) to -1.45 V vs Hg/HgO (at $-52.29 \text{ mA}/\text{cm}^2$) the sequential decline of potentials led to a reshaped IF electrode surface, changing from a dendritic thread-like morphology (Figure 7a) into a more compact solid form (Figure 7d). It is noted that the deposition of Zn ions at lower potentials was least affected by hydrogen evolution and occurred at a higher rate; hence, a more uniform surface was observed (Figure 7d). At a potential of -1.60 V vs. Hg/HgO, the deposition of Zn ions developed the dendritic form of fibers (Figure 7a). At the potential of -1.50 V vs. Hg/HgO (at $-140.86 \text{ mA}/\text{cm}^2$), the surface was further covered with deposited substances; nevertheless, the individual particulate features can still be distinguished on the surface (Figure 7b). Lower potentials of -1.50 and -1.45 V vs. Hg/HgO induced further deposition of Zn ions, resulting in a relatively craggy appearance of the anode surface (Figure 7c,d). The SEM results were compared to Zn ions deposition on a structured porous surface of NF as presented in Figure 8. Thus, it was confirmed that, at higher potentials, Zn ions were distributed within the pores of the 3D scaffold structure of the bare NF, in the form of dendrites (Figure 8a). However, the deposition of Zn at lower potentials seemed to occur, in a regular fashion, with a three-dimensional growth inside the pores and, therefore, begins to develop a compact surface on the electrode (Figure 8c,d). Similar evolution on the texture of NF, as the result of electrodeposition, has been reported previously [42].

Figure 6. CV curves at different scan rates (5 to 20) mV/s vs. current density for (a) Zn/IF and (b) Zn/NF electrodes in an electrolyte solution. Logarithmic current density peaks vs. logarithmic square root of scan rate with fitted line for (c) Zn/IF and (d) Zn/NF.

Figure 7. SEM micrographs of the Zn/IF surface (200×), at deposition potentials of (a) −1.60 V vs. Hg/HgO, (b) −1.55 V vs. Hg/HgO, (c) −1.50 V vs. Hg/HgO and (d) −1.45 V vs. Hg/HgO for 30 min in an electrolyte solution.

Figure 8. SEM micrographs of the Zn/NF surface (200 $\times$), at deposition potentials of (a) -1.60 V vs. Hg/HgO (inset 1000 $\times$), (b) -1.55 V vs. Hg/HgO, (c) -1.50 V vs. Hg/HgO and (d) -1.45 V vs. Hg/HgO for 30 min in a (1 M) Zn sulfate electrolyte solution.

The application of the IF anode exhibited different characteristics of Zn ions deposition as well as dendrite formation along the thin and straight fibers, at slightly higher levels of current density.

EDX analysis, as shown in Figures S2 and S3, confirms the presence of Zn elements after electrodeposition on both electrode surfaces, indicating that Zn deposition increases at higher current densities/lower potentials. Furthermore, BET analysis revealed that Zn electrodeposition, at a potential of -1.45 V. vs. Hg/HgO for the duration of 30 min in a (1 M) ZnSO₄ electrolyte solution, caused an increase in the surface area of both electrodes, from 0.07 and 1.20 m²/g to 0.90 m²/g and 4.09 m²/g for IF and NF substrates, respectively (see Table S1).

The results of electrochemical analysis indicated that the Zn/IF electrode performed in a similar manner to the conventional Zn/NF electrode. According to CV analysis, the Zn/IF electrode revealed a comparable mechanism of Zn dissolution/deposition with the Zn/NF electrode. Although the surface of Zn/IF is susceptible to corrosion via hydrogen evolution, the impact can be diminished when using additives to the electrolyte solution [32]. Furthermore, the IF electrode displayed a noticeably low charge transfer resistance and, hence, proved to be a preferable substitute to the conventional NF in the synthesis of the porous anode.

3.2. Performances of Zn Electrodes in a ZAB

The electrostatic charge/discharge performance of Zn/IF electrode was evaluated for cyclic stability and cycle lifespan using a ZAB. For a more precise observation, the results were compared with the performance of a Zn/NF electrode in a very similar experimental condition. Basically, the extended cycling performance of the ZAB was investigated when the cell was charging with a constant current of 10 mA/cm² for 160 s followed by resting for 60 s and then discharging under a constant current density of 10 mA/cm² to a cut-off voltage of 0.8 V. The CE and round-trip efficiency (RTE) were

calculated accordingly within 200 cycles. In Figure 9 the results are presented. For both electrodes, CE remained between 64% and 85% with average values of 78% and 80% for Zn/IF and Zn/NF, respectively. The fluctuated values of CE can be ascribed to ZnO precipitation and zincate ions crossover, which could impede overall rechargeable performance. Furthermore, the energy efficiency of Zn/IF (~39% on average) is slightly less than that of Zn/NF (~43% on average). This may be due to the sluggish kinetics of redox reaction corresponding to the higher internal resistance of Zn/IF, which eventually hinders energy output and decreases RTE.

Figure 9. The coulombic efficiency (CE) and round-trip efficiency (RTE) of electrostatic charge/discharge performance of a ZAB with Zn/IF and Zn/NF anodes within 200 cycles.

Typically, improving the solubility of ZnO in KOH can increase the average RTE and reduce the passivation of the Zn anode in an alkaline electrolyte [38]. As reported in a previous study, for a ZAB, RTE was enhanced through a newly designed catalytic dual-layer of a composite oxygen electrode, which could accelerate and catalyze the reaction of oxygen evolution at a lower potential range and achieved an RTE of 72.2% [43].

Figure 10 demonstrates that both electrodes generated stable and coincident charge/discharge profiles, similar to a typical ZAB having a porous Zn anode [44]. At the 50th and 100th cycle, the Zn/IF electrode exhibited a relatively lower discharge potential than the Zn/NF electrode as well as a lower capacity, in a shorter discharge period, resulting in a totally lower discharge performance. However, at the 200th cycle, the capacity of the battery with the Zn/IF electrode almost reached 1.48 mAh comparable to the Zn/NF electrode, at the same discharge period. Moreover, the intensive rise in charge potential and noticeably low capacity of the Zn/NF electrode in the 1st cycle can be ascribed to the instantaneous generation of hydrogen gas at the electrode/electrolyte interface. It was also observed that there were voltage plateaus in the charge/discharge curves. However, the shorter plateaus of the discharge curves can be attributed to the ZnO (that is formed during the discharge process) that acted as an insulator and passivated the Zn surface, thereby increasing the internal resistance of the battery [45].

Furthermore, the effect of charge–discharge cycling on the internal resistance of electrodes were investigated. Multicycle CV was implemented at a scan rate of 0.07 mV/s at vertex potentials ± 0.5 V vs. OCV for each electrode, in an electrolyte solution. A pure Zn plate of $1 \times 1 \text{ cm}^2$ was used as counter electrode. An open cell was employed to ensure that the generated hydrogen gas consistently discharged from the cell, thereby not imposing additional resistance at the electrodes/electrolyte interface. After every 50th cycle, the CV measurement was interrupted and EIS analysis was performed

at a frequency range from 100 kHz to 0.1 Hz with an alternate current amplitude of 10 mV around OCV; for Nyquist and Bode plots, see Figure S4a–f. In Figure 11a,b, Nyquist plots are shown at the initial state and at the 200th cycle. The equivalent circuit also used for fitting of the EIS plots and the fitted data for all circuit elements is shown in Table 3. The presence of an inductive part (L) at high frequencies is commonly related to the cables and connections [46]. The values of R_s were found to be relatively low for both cells after 200 cycles ($<3 \Omega$), indicating a high electrochemical cycling stability presented by both electrodes. The increased R_s after 200 cycles corresponds to an increase in internal resistance of the electrodes. The increment of R_s occurred with a lower magnitude when Zn/NF was used ($\sim 54\%$) than when Zn/IF was used ($\sim 100\%$), indicating that the internal resistance of the latter was more affected by morphological deterioration and reduced number of Zn ions on electrode surface. Moreover, for both cells, The R_{ct} was found to be decreased after 200 cycles suggesting that the ion transfer was easily facilitated, and reversibility was improved through charge–discharge cycling. The more significant reduction of R_{ct} associated with the cell involved Zn/IF ($\sim 81\%$) than Zn/NF ($\sim 57\%$) suggests that the contact area was increased, and hence faster ion transport occurred at the electrode–electrolyte interface during charge–discharge cycling. The increased contact area can be ascribed to the less stability, and hence deterioration of passivation layer when increasing the number of cycles. The deteriorated passivation layer causes the active sites on the electrode to expose more to the electrolyte and thus enhance the kinetics of the charge transfer process.

Figure 10. Charge and discharge performances of the ZAB under 10 mA/cm^2 in electrolyte solution at the 1st, 50th, 100th and 200th cycle for (a) Zn/IF and (b) Zn/NF electrodes.

Figure 11. Nyquist plots of cycling impact on cell impedance when using (a) Zn/IF and (b) Zn/NF electrodes at the initial state ($t = 0$) and after the 200th charge–discharge cycle at a frequency range from 100 kHz to 0.1 Hz with an alternate current amplitude of 10 mV around OCV.

Table 3. Resistance values of Zn anodes in the electrolyte at initial state ($t = 0$) and after the 200th charge–discharge cycle.

Component	Zn/IF ($t = 0$)	Zn/IF (200th Cycle)	Zn/NF ($t = 0$)	Zn/NF (200th Cycle)
$L \times 10^7 (\Omega)$	2.065	1.874	2.197	2.149
$R_s (\Omega)$	1.489	2.967	1.142	1.761
$R_{CT} (\Omega)$	8.220	1.510	7.500	3.205

4. Conclusions

In this work, it was noted that substituting the conventional NF with IF, as an anode current collector for ZABs, was found to be feasible. This was because it performed with almost comparable electrochemical properties as NF. According to EIS analysis, the use of Zn/IF was found to improve the charge transfer of the anode. Potentiodynamic polarization revealed that IF reduced the rates of anode reactions and it was effective in decreasing the corrosion susceptibility of the Zn anode. All electrochemical characterization and measurements agreed that the Zn/IF electrode was able to compete with the conventional NF-based electrode in terms of performance and characteristics. When used in a ZAB, IF exhibited a relatively comparable charge/discharge performance to the NF electrode. The Zn/IF electrode exhibited comparable CE and RTE to the Zn/NF electrode. Moreover, the evolution of electrode impedance with charge–discharge cycling was investigated and the results of EIS revealed that Zn/IF could significantly reduce the charge transfer resistance after 200 cycles, even at a higher magnitude than the Zn/NF electrode. Thus, considering its lower cost, the Zn/IF electrode was found to be a valuable replacement for NF in the fabrication of ZABs.

Supplementary Materials: The following are available online at <http://www.mdpi.com/1996-1073/13/6/1429/s1>, Table S1: Surface area, pore volume, and average pore diameter (N_2 adsorption–desorption isotherm) of different bare and anode samples. Figure S1: Bode diagrams of fitted EIS lines at a starting frequency of 100 kHz to 0.1 Hz for (a) Zn/IF and (b) Zn/NF electrode around OCV in electrolyte solution. Figure S2: EDX of zinc electrodeposition on IF at potential of (a) -1.60 V vs. Hg/HgO, (b) -1.55 V vs. Hg/HgO, (c) -1.50 V vs. Hg/HgO and (d) -1.45 V vs. Hg/HgO. Figure S3: EDX of zinc electrodeposition on NF at potential of (a) -1.60 V vs. Hg/HgO, (b) -1.55 V vs. Hg/HgO, (c) -1.50 V vs. Hg/HgO and (d) -1.45 V vs. Hg/HgO. Figure S4: Evolution of cell impedance at initial stage and after 50th, 100th, 150th and 200th charge–discharge cycle: (a) Nyquist plots when used Zn/IF, (b) Nyquist plots when used Zn/NF, (c) BOD diagram when used Zn/IF at initial state ($t = 0$), (d) BOD diagram when used Zn/IF at 200th cycle, (e) BOD diagram when used Zn/NF at initial state ($t = 0$), (f) BOD diagram when used Zn/NF at 200th cycle at a frequency range from 100 kHz to 0.1 Hz with an alternate current amplitude of 10 mV around OCV.

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Abbreviations

CV	Cyclic voltammetry
CR	Corrosion rate
CE	Coulombic efficiency
EIS	Electrochemical impedance spectroscopy
EES	Electrical energy storage system
E_{corr}	Corrosion potential
HER	Hydrogen evolution reaction
I_{corr}	Corrosion current density
IF	Iron fibers
NF	Nickel foam
ORR	Oxygen reduction reaction
RTE	Round-trip efficiency
SEM	Scanning electron microscope
ZAB	Zinc–air battery
Zn/IF	Zinc electrodeposited on iron fibers
Zn/NF	Zinc electrodeposited on nickel foam
Zn/Cu	Zinc adhered on copper plate

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