Controlling Magnesium Self-Corrosion in Mg−Air Batteries with the Conductive Nanocomposite PANI@3D-FCNT

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ABSTRACT: A promising potential device for storage of large amounts of energy is Mg−air batteries. However, the corrosion of the Mg electrode inside the battery electrolyte limits the battery’s capacity to store energy. We present a new strategy to protect the Mg electrode from corrosion and increase the life cycle of Mg batteries in this article. The Mg electrode is coated with a conductive nanocomposite (PANI@3D-FCNT) in this technique. To better understand the anticorrosion properties of PANI@3D-FCNTs and their effect on the battery efficiency, electrochemical and battery tests are used. We discovered that PANI@3D-FCNT plays the most promising role in reducing Mg electrode corrosion in 3.5 wt % NaCl electrolyte, with an efficiency of 93.9%. The battery with the coated Mg electrode has a longer discharge time and a slower drop in operating voltage. The PANI@3D-FCNT nanocomposite will prolong the life of the Mg−air battery and keep the Mg electrode active for a long time. This work outstandingly provides an effective strategy to address the defects in the Mg−air batteries arising from electrode corrosion successfully. The work is a great way to open up new avenues for introducing new conductive nanocomposites in metal−air battery designs without using traditional methods.

1. INTRODUCTION

Mg−air batteries will be urgently demanded in the coming future.1−3 This is due to their features such as high abundance, low cost, and nontoxicity compared to the lithium batteries.4 The major problem here is the contact between the Mg electrode and the corrosive battery electrolyte (3.5% NaCl solution), leading to the Mg corrosion.5,6 Li et al.7 indicated that the formation of MgO or MgO2 layer on the surface of the Mg electrode during the battery discharge leads to the loss in battery capacity, where Mg oxides work as an insulating cover for the Mg electrode. In addition, Mg oxides increase electrode polarization.

Several researchers attempted to develop alloy Mg with different elements such as, Ga, Zn, Hg, and Al.8−10 The alloying elements help the Mg electrode by shifting its polarization in the negative direction and decreasing self-corrosion. This is clearly seen from the Wang et al. work,11 where they found that the use of Mg/Al/Pb/In alloy leads to high battery performance compared with pure Mg.

Electrolyte additives were used by many researchers to overcome the Mg self-corrosion problems in Mg−air batteries. Mayilvel Dinesh et al.12 used the water-soluble graphene to control Mg self-corrosion in the battery electrolyte. They indicated that the addition of water-soluble graphene into 3.5% NaCl solution leads to high self-corrosion resistance and high discharge capacity. Deyab13 also used decyl glucoside as electrolyte additives. He found that decyl glucoside improved the discharge capacity and anodic utilization of the battery. In this case, the decyl glucoside was able to suppress the Mg self-corrosion and prevent the coverage of the Mg by Mg oxides.

Here, our work lights the way to use a new strategy based on using the conductive nanocomposite (PANI@3D-FCNT) to coat the Mg electrode and to protect the Mg electrode from corrosion. The polyaniline (PANI) and three-dimensional functionalized carbon nanotube (3D-FCNT) are the main components of the conductive nanocomposite (PANI@3D-FCNT). Specifically, we aim to increase the lifetime for Mg−air batteries using a coated Mg electrode by the PANI@3D-FCNT nanocomposite.

2. RESULTS AND DISCUSSION

2.1. Morphology Characterization. The morphology of the PANI@3D-FCNT nanocomposite was characterized with scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectra, as shown in Figure 1.
The SEM and TEM images indicated that the outer surface of a FCNT is completely covered by PANI. Precisely, PANI is wrapped in a single-dimensional core–shell nanostructure around the FCNT. The Raman peaks of FCNT (i.e., D and G peaks) appear around 1348 and 1587 cm$^{-1}$, respectively. The Raman peaks of PANI@3D-FCNT appear around 1162, 1310, 1348, 1470, and 1696 cm$^{-1}$. This means that all characteristic peaks of PANI are presented in the Raman spectrum of PANI@3D-FCNT. We noted also that the intensity of FCNT peaks in the Raman spectrum of PANI@3D-FCNT decreased compared with neat PANI. The reason is attributed to the coverage of the FCNT surface by PANI.

2.2. Anticorrosion Property of PANI@3D-FCNT Nanocomposites.

In order to investigate the anticorrosion property of PANI@3D-FCNT nanocomposites, we employ polarization curves for bare and composite-coated Mg electrodes in a 3.5 wt % NaCl electrolyte to explore the correlation of the presence of the nanocomposite with the corrosion rate of the Mg electrode (see Figure 2).

As shown in Figure 2, a clear shift in the anodic and cathodic Tafel lines occurs when Mg electrodes were coated with PANI and PANI@3D-FCNT nanocomposites. In detail, we extracted the polarization parameters (i.e., corrosion potential $E_{\text{corr}}$—corrosion current density $j_{\text{corr}}$) for all polarization experiments to compare the efficiency quantitatively. The $j_{\text{corr}}$ is calculated using Tafel extrapolation of polarization curves in Figure 2.

In the case of bare Mg, the $j_{\text{corr}}$ is $8.9 \times 10^{-4}$ A cm$^{-2}$ and $E_{\text{corr}}$ is $-1.596$ V. After PANI-coated Mg is used, the $j_{\text{corr}}$ decreased to $1.99 \times 10^{-4}$ A cm$^{-2}$ and $E_{\text{corr}}$ shifted to $-1.332$ V. Significantly, after composite-coated Mg is used, the $j_{\text{corr}}$ decreased to $0.63 \times 10^{-4}$ A cm$^{-2}$ and $E_{\text{corr}}$ shifted to $-1.151$ V.

Based on the above results, the anticorrosion efficiency of PANI@3D-FCNT nanocomposites ($\eta$ %) was calculated using the following relation:

$$\eta \% = \frac{j_{\text{corr(uncoated)}} - j_{\text{corr(coated)}}}{j_{\text{corr(uncoated)}}} \times 100$$

The $\eta$ % could be calculated to be 77.6% for PANI-coated Mg and 93.9% for composite-coated Mg. This confirms the anticorrosion property of the PANI@3D-FCNT nanocomposite. When compared to other materials described in the literature for magnesium in NaCl solutions, this result confirms the remarkable anticorrosion characteristic of PANI@3D-FCNT (see Table 1).

AC electrical measurements normally give greatly more data on coatings and undercoating film corrosion processes than
DC measurements. To explore the electrochemical impedance (AC data) properties of bare and coated Mg electrodes in 3.5 wt % NaCl electrolyte (the time of immersion is 7 days), Nyquist and Bode-phase angle plots were recorded, as shown in Figures 3 and 4.

The Nyquist plots (Figure 3) for bare and coated Mg electrodes are characterized by two-time constants. In the Bode plots (Figure 4), the two-time constants are seen but less remarkable on these plots. The loop at high frequency corresponds to the coating and/or oxide layer. The loop at low frequency corresponds to the corrosion of Mg electrodes in 3.5 wt % NaCl. As shown in Figure 4, the PANI@3D-FCNT coating exhibits the widest phase angle over a wide range of frequencies, signifying that it has the strongest barrier function to the corrosive electrolyte. The equivalent circuit (EC) describes this impedance response, as presented in Figure 5.

In this EC, coating resistance ($R_c$) appears parallel to coating capacitor ($C_c$). Due to the corrosion of Mg electrodes in 3.5 wt % NaCl, additional EC elements ($R_{ct}$ charge transfer resistance and $C_{dl}$ double-layer capacitance) arise in series with the coating elements. $R_{ct}$ is linked to the corrosion rate of the Mg electrodes, and $C_{dl}$ is linked to the contact between the electrolyte and the Mg surface.

In details, the $R_{ct}$ increases in the following order: composite-coated Mg ($2453 \, \Omega \, cm^2$) > PANI-coated Mg ($1253 \, \Omega \, cm^2$) > bare Mg ($365 \, \Omega \, cm^2$). Compared to PANI-coated Mg ($R_e = 1056 \, \Omega \, cm^2$), the use of PANI@3D-FCNT nanocomposite increases the $R_e$ to $\sim 1840 \, \Omega \, cm^2$. The data confirm that this PANI@3D-FCNT nanocomposite is becoming increasingly impermeable with time, with a significant high of anti-corrosion properties.

To confirm this assumption, the information about the coating permeability is obtained from the determination of the initial coating capacitor ($C_c$) and the coating capacitor at end of the experiment (i.e., time) ($C_c'$) using the following relation

$$\phi \% = \left[ \log\left(\frac{C_c'}{C_c}\right) / \log(eH_2O) \right] \times 100$$

Figure 6 compares the volume fraction of H$_2$O ($\phi$ %) absorbed by neat PANI and PANI@3D-FCNT nanocomposite at different time intervals. In the case of neat PANI coating, the $\phi %$ increased linearly until up to $\sim 14$ days and reached 11.16% and then maintained at $\sim 11.51%$ after 30 days. Compared to neat PANI coating, the use of PANI@3D-FCNT nanocomposite decreased the $\phi$ % to $\sim 1.2%$ at initial days (i.e., $\sim 5$ days) and then maintained at $\sim 1.3%$ after 30 days. These results highlight that 3D-FCNT nanoparticles are effectively reducing the coating porosity and remain stable over a long time.

2.3. Mg−Air Battery Performance. Figure 7 displays the discharge behavior of Mg−air battery using bare Mg and coated Mg electrodes at a current density of 1.0 mA cm$^{-2}$. In the case of bare Mg electrode, the operating voltage of the Mg−air battery dropped rapidly in the early discharging time. This is due to the corrosion of bare Mg electrode in the battery.

### Table 1. Comparison of the Inhibition Efficiency of PANI@3D-FCNT Nanocomposite with Other Materials Reported in the Literature for Magnesium in NaCl Solutions

| compounds                        | metal          | solution                  | efficiency % | refs |
|----------------------------------|----------------|---------------------------|--------------|------|
| hydroxylethyl cellulose          | AZ31 Mg alloy  | 3.5 wt % NaCl             | 80.5         | 18   |
| orange peel extracts             | AZ91D Mg alloys| 0.05 wt % NaCl            | 85.7         | 19   |
| stearate                         | ZE41 Mg alloy  | 0.2 M Na$_2$SO$_4$−0.1 M NaCl | 88.0         | 20   |
| benzyl triphenyl phosphonium bis(trifluoromethylsulfonyl)amide | AZ31B Mg alloy | 0.05 wt % NaCl | 91.4 | 21   |
| tetraphenylporphyrin             | AZ91D Mg alloy | 0.05 wt % NaCl            | 90           | 22   |
| PANI@3D-FCNT                     | Mg             | 3.5 wt % NaCl             | 93.9         | this work |

Figure 3. Nyquist plots of bare and coated Mg electrodes in 3.5 wt % NaCl electrolyte at 298 K.

Figure 4. Bode-phase angle plots of bare and coated Mg electrodes in 3.5 wt % NaCl electrolyte at 298 K.

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PANI matrix reduced the total pore volume of the PANI@3D-FCNT method verifying the anticorrosion efficiency of the PANI@3D-FCNT nanocomposite to 93.9% and \( R_{ct} \) to \( \sim 1840 \Omega \text{ cm}^2 \).

Because PANI@3D-FCNT nanocomposite coating can protect the Mg electrode from corrosion and prevents the covering of the Mg electrode by oxides, the Mg–air battery lifetime became longer compared with the bare Mg electrode. 3D-FCNT nanoparticles are characterized by very high surface area with the three dimensions (BET surface area = 172.6 m\(^2\) g\(^{-1}\)), in addition, the functional groups attached with the CNT surface facilitate high-speed electron transfer and are conductive inside the PANI matrix. All of these features facilitate the distribution of 3D-FCNT inside the PANI matrix and increase the contact adhesion between the Mg electrode and coating. Moreover, 3D-FCNT nanoparticles improve the electrochemical conductivity of battery electrodes, leading to a high-performance Mg–air battery with a long lifetime.

3. CONCLUSIONS

In brief, we successfully prepared the PANI@3D-FCNT nanocomposite to protect the Mg electrode from corrosion in 3.5 wt % NaCl and increase the lifetime of the Mg–air battery. This represents a new strategy in the field of Mg–air batteries. The PANI@3D-FCNT nanocomposite is based on PANI and 3D-FCNTs. The corrosion rate of the Mg electrode using PANI@3D-FCNT can generally be decreased by 93.9% compared with the bare Mg electrode. The incorporation of 3D-FCNT inside the PANI matrix leads to a decrease in the porosity of the PANI. In addition, PANI@3D-FCNT improves the electrochemical conductivity of battery electrodes, leading to a high-performance Mg–air battery with a long lifetime. Our strategy for developing PANI@3D-FCNT nanocomposites holds broad promise for Mg–air battery applications by increasing the lifetime of the Mg–air battery electrode and maintaining the electrochemical activities for a long time.

4. MATERIALS AND METHODS

4.1. Materials. Magnesium rod (99.8%) was purchased from Alfa Aesar. Analytical type NaCl (PubChem) and distilled H\(_2\)O were used to prepare the battery electrolyte (3.5 wt % NaCl). PANI, dimethylformamide (DMF), thionyl chloride (SOCl\(_2\)), and N-methyl-2-pyrrolidone azobisobutyronitrile (AIBN) were purchased from Sigma-Aldrich Co. CNTs were prepared by EPRI (Egypt) lab.

4.2. Preparation of the 3D-FCNT and PANI@3D-FCNT. CNTs were oxidized with a mixture of H\(_2\)SO\(_4\) and HNO\(_3\) (v/v = 3:1) (conditions: sonication at 323 K for 3 h). FCNT (CNT–COOH) was separated out, washed, and then dried. The CNT–COOH was changed to CNT–COCl by reacting with SOCl\(_2\). CNT–COCl was then converted into CNT–NH\(_2\) by reacting with DMF at 343 K for 24 h. 3D-FCNTs were produced by free-radical polymerization of nanotube monomers in DMF using AIBN followed by sonication and freeze-dried in liquid nitrogen and then dried.

The PANI@3D-FCNT was prepared using the direct solid-state mixing method. 1.0 g of PANI and 0.12 g 3D-FCNT were mechanically blended using a laboratory mortar mixer for 2.0 h to get the required fineness. The powered PANI@3D-FCNT was dissolved in NMP by mixing at 323 K for 2.0 h and sonication for 3 h. The morphology of the PANI@3D-FCNT was
inspected using SEM (Model Quanta/250, FEI Company), TEM (Jeol-Jem 1200EX II equipped with TEM), and Raman spectroscopy (Jasco FT-Raman 6000 spectrometer). Total pore volume and surface area of the pure 3D-FCNT and PANI@3D-FCNT were determined using the BET method (Quantochrome NOVA Station A).

PANI@3D-FCNT nanocomposite coating was applied on the Mg electrode surface using a spray gun (Walther PILOT Co). The coated Mg electrodes were cured at 333 K for 3.0 h. For comparison purposes, the coated Mg electrode by neat PANI was prepared under the same conditions but without 3D-FCNT.

4.3. Electrochemical and Battery Performance Measurements. The anticorrosion activities of PANI@3D-FCNT nanocomposite coating were assessed using polarization and electrochemical impedance spectroscopy (EIS) methods. The polarization curves were registered with a scan rate of 1.0 mV s⁻¹ and potential range of ±250 mV versus OCP. EIS plots were registered in the frequency range 1.0 Hz to 30 kHz at the OCP and 10 mV amplitude. All electrochemical measurements were conducted using three electrode (Mg, Ag/AgCl, and Pt) cell connected with the electrochemical work station potentiosist (Gamry 3000 Instruments, Inc.).

The permeability of PANI and PANI@3D-FCNT nanocomposite coatings is obtained from the determination of the initial coating capacitor and the coating capacitor at end of the EIS experiments. The performance of the Mg–air battery with bare Mg and coated Mg electrodes at a current density of 1.0 mA cm⁻² was evaluated using the laboratory battery previously described by Deyab.13

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