

## Research Article

# Novel Method for Floating Synthesizing Heavy Metal Particles as Floating Anode of Zinc-Air Fuel Cell

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In this study, centrally hollow microspheres of zinc were synthesized. The microspheres were then mixed with KOH electrolyte to form zinc sol, which was coagulated and precipitated. Afterward, we employed a novel technique to enable the permanent floating of zinc particles, which involved stirring zinc sol with air using a magnetic stirrer. This resulted in the formation of foam in which the zinc particles permanently floated. We then added 65 wt% of the electrolyte (KOH) to prepare 35 wt% of zinc sol. We tested the cell and found the values of current density, specific energy, and electric capacity to be 7.41 mA/cm<sup>2</sup>, 840.14 Wh/kg, and 3023 mAh, respectively.

## 1. Introduction

Currently, the technologies used for shale oil refining, methane clathrate mining, and oil excavation in the melting waters of the Arctic Ocean are being widely promoted. However, horizontal drilling and hydraulic fracturing could trigger earthquakes and pollute the groundwater. Also, the emissions resulting from burning oil, hydrocarbons, CO, CO<sub>2</sub>, and NO<sub>x</sub> pollute the environment and amplify the greenhouse effect, thereby increasing the likelihood of global disasters [1].

The zinc-air fuel cell could be a source of clean energy owing to its simplicity, high efficiency, high energy density, high power density, low operating temperature, low cost, and environment friendliness.

In this study, we began with feeding the fuel manually into the zinc-air fuel cell. However, we soon realized that if we wanted to feed the fuel continuously, the anode would have to be modified from a solid state to a fluid state. Therefore, it was necessary that the zinc particles float.

In 2001, Colborn and Smedley proposed the concept of a zinc-air fuel cell system and single fuel cell management [2]. In their single fuel cell, the zinc pellets were introduced on the top of the zinc electrode, and then circulated in the electrolyte using a pump. The air was blown using a blower into the electrolyte in a top-down manner (Figure 1).

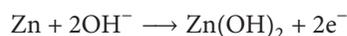
In our study, the zinc particles, which were mixed with the KOH electrolyte, were aggregated and precipitated. The aggregation increased with the increasing concentration of KOH.

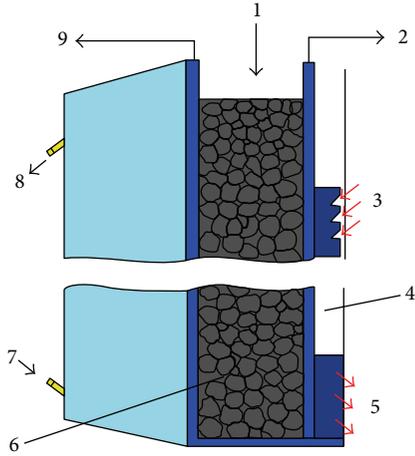
The micelle technology was used to generate chemical particles whose sizes were consistent with those of the polymer microspheres. Next, the chemical modification of the surface functional groups afforded the reduction and hence deposition of the silver and zinc particles on the surface of the microspheres.

We mixed the microspheres with the electrolyte to form zinc sol, which was then floated and flown through a porous current collector using an electrolyte circulation system, thus resulting in a fluid anode. By incorporating appropriate fuel fluidity and current collection, the design and performance of the zinc-air fuel cell were improved.

## 2. Working Principle

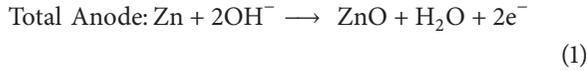
In the zinc-air fuel cell, the zinc metal is oxidized, releasing chemical energy in the form of electrical energy [3]. The anode reaction is as follows:





- |  |                                   |
|--|-----------------------------------|
| (1) Zinc pellets introduced into top of zinc electrode | (6) Zinc electrode (zinc pellets) |
| (2) Positive terminal                                  | (7) Electrolyte in                |
| (3) Air inlet from air blower                          | (8) Electrolyte out               |
| (4) Air electrode                                      | (9) Negative terminal             |
| (5) Air outlet   |                                   |

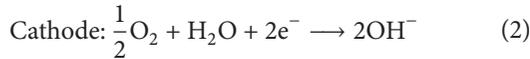
FIGURE 1: Metallic power company cell.



$$E^0 = 1.25 \text{ V.}$$

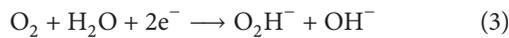
The existence of zincate species containing  $\text{Zn}^{2+}$  such as  $\text{ZnO}$ ,  $\text{Zn(OH)}_2$ ,  $\text{ZnO}_2^{2-}$ , and  $\text{Zn(OH)}_4^{2-}$  depends on the temperature and concentration of  $\text{OH}^-$  and supersaturation of zincate.

The oxygen can be reduced to hydroxyl ions according to the following reaction:



$$E^0 = 0.40 \text{ V.}$$

However, direct electrochemical (four-electron) reduction to hydroxide ions described in (2) will occur only in the presence of special catalysts. In the absence of such a catalyst (e.g., on the surface of carbon substrate), the electrochemical (two-electron) reduction to peroxide ions dominates as the cathodic reaction of the zinc-air battery, as shown in the following equation:



The resulting peroxide ions are generally unstable and get decomposed via the disproportionation reaction of oxygen to produce hydroxide ions and molecular oxygen, as shown

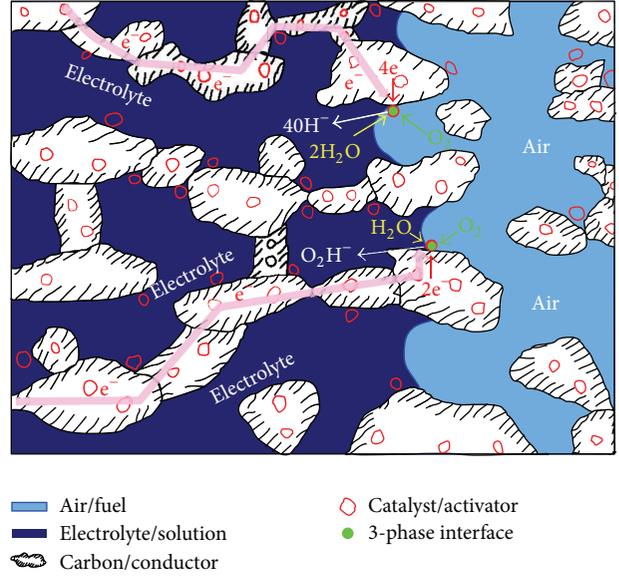
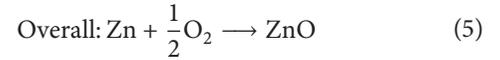
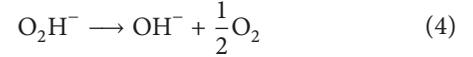


FIGURE 2: Three-phase interface within catalyst of zinc-air fuel cell.

in (4). The schematic of the catalytic reaction involving interactions with three phases is shown in Figure 2 [4],



$$E^0 = 1.65 \text{ V.}$$

The reaction schemes are shown in Figures 3 and 4.

The equation pertaining to the conversion of chemical energy to electrical energy is mentioned below:

$$E_r = \frac{-\Delta G}{nF}, \quad (6)$$

$$E = E^r - \eta_{\text{all}}$$

$E_r$ : voltage between anode and cathode,  $\Delta G$ : free energy change,  $n$ : electronic number,  $F$ : Faraday constant,  $E$ : discharge voltage, and  $\eta_{\text{all}}$ : overvoltage.

In general, in terms of the condition of overvoltage ( $\eta_{\text{all}}$ ), three phenomena are observed in zinc-air fuel cells: activation overvoltage, concentration overvoltage, and ohmic overvoltage. These three phenomena also serve as the best standards to determine the quality of cells (Table 1).

According to the IUPAC definition, a colloidal particle retains its properties within the range 1–1000 nm in the three-dimensional space.

The solution of colloidal particles (dispersed phase) dispersed in a solvent molecule (dispersion medium) is called a colloidal solution. A colloidal dispersion solution is depicted in Table 2 [5].

Sol phenomenon: collisions due to the thermal motion of the solvent molecules containing the particles result in an

TABLE 1: Causes of three types of overvoltage and their solutions.

	Cause	Solution
Activation overvoltage	If $\text{HO}_2^-$ ions are absorbed on the electrode surface, the reaction mechanism by which $\text{O}_2$ changed to $\text{OH}^-$ ions will slow down. This leads to activation polarization and results in activation overvoltage	Elevate the temperature of a cell, as well as the reaction speed of three-phase boundaries
Concentration overvoltage	Because of poor gas diffusion, $\text{O}_2$ supply in the reaction becomes too slow; as a result, $\text{O}_2$ concentration becomes insufficient. This causes concentration polarization and results in concentration overvoltage	Elevate the flow speed of $\text{O}_2$ at the anode and increase the $\text{O}_2$ concentration
Ohmic overvoltage	Because of improper design, poor conductivity of electrolytes or impurities in the electrodes increasing resistance to current flow, ohmic polarization may occur, resulting in ohmic overvoltage	Use electrode materials and electrolytes with higher conductivity

TABLE 2: Types of colloidal dispersion.

Dispersed phase	Dispersion medium	Name
Solid	Solid	Solid suspension
Solid	Liquid	Sol, colloidal suspension; paste (high solid concentration)
Solid	Gas	Solid aerosol
Liquid	Solid	Solid emulsion
Liquid	Liquid	Emulsion
Liquid	Gas	Liquid aerosol
Gas	Solid	Solid foam
Gas	Liquid	Foam

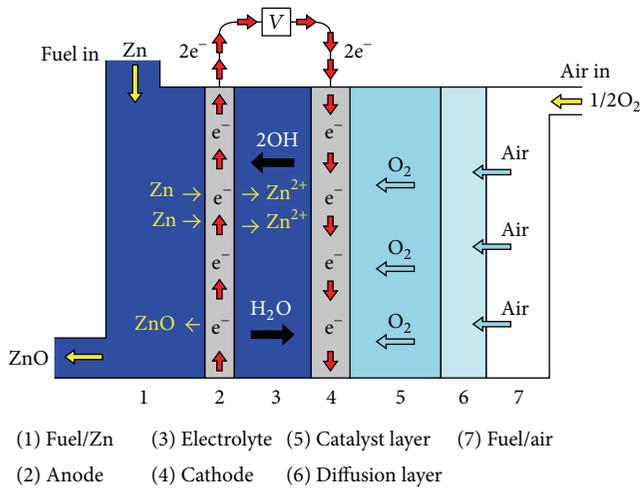


FIGURE 3: Working schematic of zinc-air fuel cell.

uneven force in all directions. Therefore, a Brownian movement is created, which results in the coagulation of colloids.

The colloidal particles in the electrolyte solution or such other polar solution undergo mechanisms such as ionization, ion adsorption, and ion dissolution to generate surface charges. This attracts the adjacent, oppositely charged ions (counter-ion) in the solution to the particle surface and repels

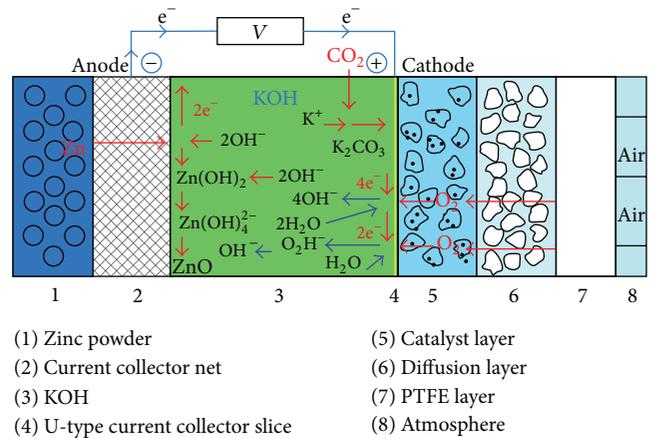


FIGURE 4: Reaction schematic of zinc-air fuel cell.

ions with the same charge (coion) away from the particle surface.

Therefore, the condition of charge distribution from the surface of the colloidal particles to the solution is called electric double layer.

Because of Brownian motion, colloidal particles undergo successive collisions with other particles.

- (1) If the repulsion between the particles is smaller than the force of gravity, the particles, after colliding with each other, will permanently integrate and form collectives. This phenomenon of precipitation of colloidal particles is called coagulation.
- (2) If the repulsion between the particles is larger than gravity, the particles, after colliding with each other, will remain dispersed in the solution in an individual state. Such colloidal particles remain suspended in the solution [6, 7].

When the particle diameter is  $<5 \mu\text{m}$ , it will be influenced by the Brownian motion.

Because charged colloidal particles in suspension repel each other through the electric double layer, they can stably float in solution without coagulation. If a salt-based electrolyte is added to the solution, it will destroy the electric

double layer and reduce the electric repulsion between the particles, thereby coagulating the colloidal particles [8–10].

The colloidal stability is determined by the electrostatic repulsion and van der Waals forces between the particles [11].

The van der Waals force  $F_v$ :

$$F_v = \frac{k_v r}{16\pi R^2} \quad (7)$$

$F_v$ : van der Waals force,  $k_v$ : van der Waals constant,  $r$ : particle radius, and  $R$ : distance between two particles.

### 3. Experimental

**3.1. Precipitation of Zinc Particles.** The critical barriers for establishing a fluid electrode include precipitation of zinc particles, cluster aggregation of the zinc paste, and congestion of the current collector.

We attempted to float the zinc particles using dispersants carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA), and polyacrylic acid sodium (PAAS), but in vain.

- (1) When only zinc particles were mixed with water, the dispersion of zinc (fluid effect) was achieved. The flowing time was very short; for a short time interval, no stirring was carried out. As a result, although the precipitation of zinc started, it did not cascade to aggregation. On the other hand, when the zinc particles were added to water containing KOH, zinc particles showed significant aggregation and thus precipitation, which increased with the increasing concentration of KOH.
- (2) Then, 30 wt% zinc powder was mixed with 30 wt% KOH electrolyte; as a result, aggregation and precipitation occurred.
- (3) Next, 20 wt% KOH was mixed with 3 wt% CMC, followed by mixing with 30 wt% zinc; as a result, there was significant aggregation followed by precipitation.
- (4) Subsequently, 20 wt% KOH was mixed with 3 wt% PVA, followed by mixing with 30 wt% zinc; as a result, there was significant aggregation followed by precipitation.
- (5) Finally, 20 wt% KOH was mixed with 3 wt% PAAS and then added to 30 wt% zinc; as a result, there was neither aggregation nor precipitation. However, as the KOH concentration was increased to 30 wt%, the effect of zinc was completely lost because all the zinc particles settled at the bottom (sedimentation), and aggregation did not occur.

Floating test of centrally hollow zinc microspheres.

Surfactants are amphiphilic compounds. Their molecular structure mainly comprises hydrophilic groups (polar or ionic moieties) and hydrophobic groups (nonpolar hydrocarbon chains).

When the concentration of the surfactant in the solution is very low, it is usually present in the monomeric form. On the other hand, when the concentration of the surfactant is increased to saturation, the surfactant molecules aggregate

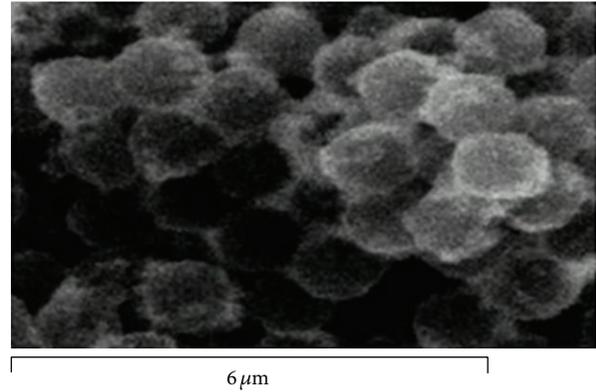


FIGURE 5: Scanning electron microscopy image of polystyrene/Ag microspheres.

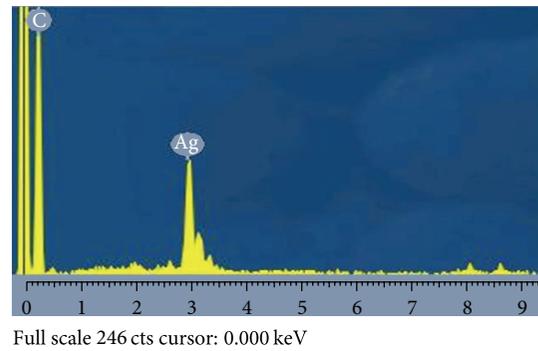


FIGURE 6: Energy-dispersive X-ray spectral analysis of polystyrene/Ag microspheres.

(tens to hundreds). The hydrophilic ends are in contact with the water molecules outwardly; such aggregates are referred to as “micelles.” When the micelles are formed, the concentration of the surfactant is called the “critical micelle concentration” (CMC).

When the surfactant was added to a water-oil system, the surface tension was reduced to about  $1 \text{ mNm}^{-1}$ , and the resulting micelle size was about  $100 \text{ \AA}$ . With such a dimension,  $\Delta S$  and  $\Delta A$  were large, but surface tension  $\gamma$  was small. However, the free energy was less than 0 ( $\Delta G < 0$ ). This indicated that the micelles were thermodynamically stable [12, 13]. By using the Gibbs free energy, we obtain the following relation:

$$\Delta G = \gamma \Delta A - T \Delta S \quad (8)$$

$T$ : temperature,  $A$ : area,  $S$ : entropy, and  $\gamma$ : surface tension.

We synthesized the centrally hollow zinc microspheres by employing the micelle technology on the zinc particles as follows [14]:

- (1) micelle emulsion microspheres  $\rightarrow$  nanopolymer microspheres;
- (2) surface modification using functional groups  $\rightarrow$  polystyrene microspheres;

TABLE 3: The experimental parameters and data of constant current electrolysis.

	Original weight (g)	After electrolysis weight (g)	Electrolysis voltage (V)	Electrolysis current (A)	Electrolysis time (min)	Stir (Y/N)	Current efficiency (%)
Sample 1	0.9323	0.9679	2.3	0.03	5	Y	0.3242
Sample 2	0.9441	0.9466	2.2	0.03	3	Y	0.0379
Sample 3	1.0618	1.0875	2.6	0.06	5	Y	0.1170
Sample 4	1.0257	1.0634	2.3	0.03	5	N	0.3434

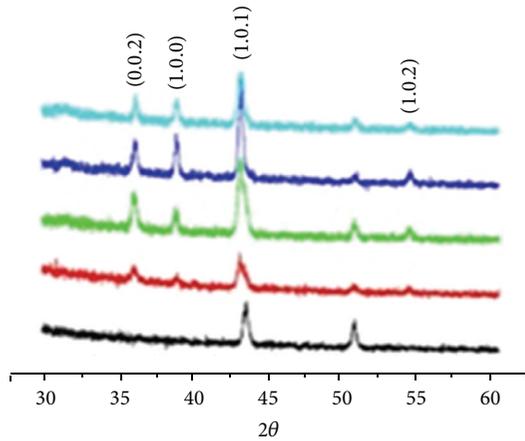


FIGURE 7: X-ray diffraction patterns of zinc metal precipitation by flow electrolysis. (a) Background, black. (b) Sample 1, red. (c) Sample 2, green. (d) Sample 3, blue. (e) Sample 4, light blue. (Unindexed peaks mean steel background signal.)

- (3) (i) current electrolysis → centrally hollow zinc metal microspheres,
- (ii) spray granulation → centrally hollow zinc metal microspheres.

The steps can be elucidated as follows.

*Step 1.* Synthesis of polystyrene (PS) microspheres using micelle technology.

*Step 2.* Surface modification by functional groups involving silver mirror reaction (PS + Ag) (Figures 5 and 6).

*Step 3.* (i) Current electrolytic zinc metal making centrally hollow zinc metal microspheres (PS + Ag + Zn) (Figures 7, 8, and 9).

The experimental parameters and data of constant current electrolysis are shown in Table 3.

(ii) Spray deposition of zinc metal making centrally hollow zinc metal microspheres (PS + Ag + Zn) (Figure 10).

#### 4. Results and Discussion

After forming the zinc particles using the micelle technology, we synthesized the centrally hollow zinc microspheres. These were then mixed with the KOH electrolyte to form the zinc sol, which coagulated and precipitated, at least initially. As the concentration of the electrolyte increased, the zinc particles became more prone to precipitation [15]. The results of the

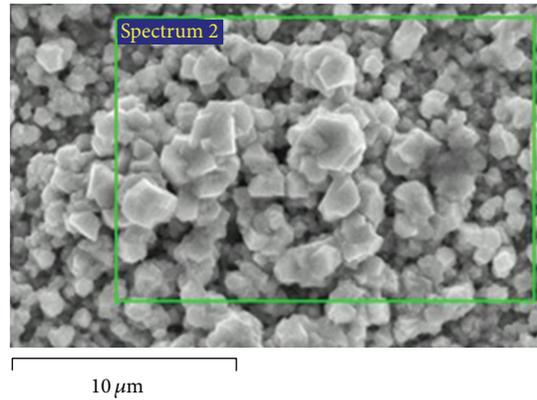


FIGURE 8: Scanning electron microscopy image of sample 1 plated layer.

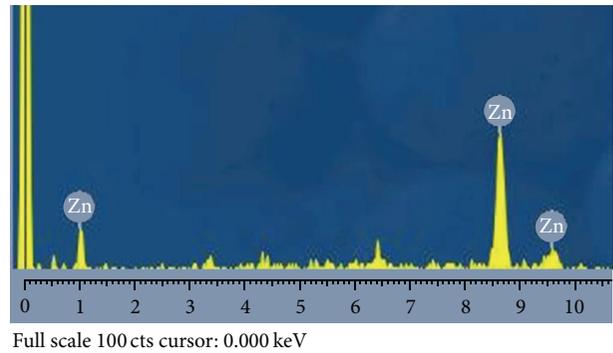


FIGURE 9: Energy-dispersive X-ray spectrum composition analysis of local region.

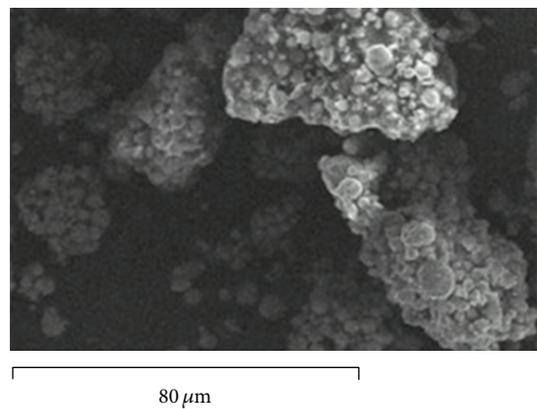


FIGURE 10: Scanning electron microscopy image with 750x magnification.

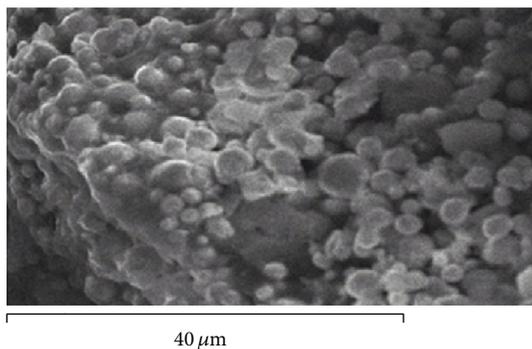


FIGURE 11: Scanning tunneling microscopy image of zinc sol.



FIGURE 12: Successful floating of zinc sol.

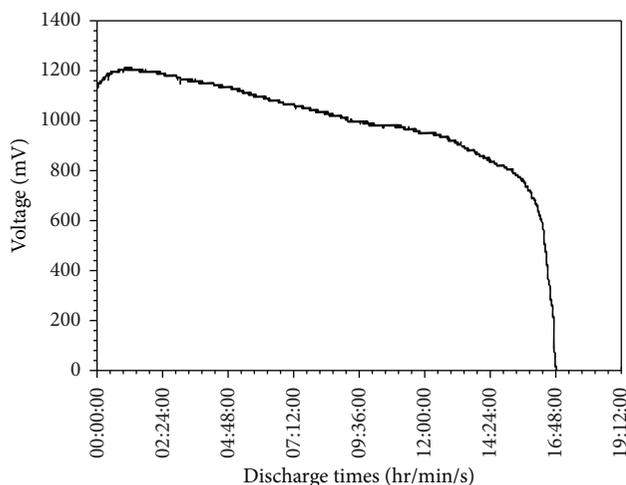


FIGURE 13: Voltage curve of 35 wt% zinc sol under a constant-current discharge at 200 mA.

scanning tunneling microscopy (STM) studies are shown in Figure 11.

Next, we added air into the zinc sol, and stirred the mixture using a magnetic bar. As a result, the zinc sol gradually foamed like a milkshake, thus enabling the permanent floating of the zinc particles [15, 16] (Figure 12).

We added 65 wt% of the electrolyte to prepare 35 wt% of the zinc sol. The cell, as Figure 13 shows, was tested under a constant-current discharge at 200 mA. The values of current density, specific energy, and electric capacity were found to be  $7.41 \text{ mA/cm}^2$ ,  $840.14 \text{ Wh/kg}$ , and  $3023 \text{ mAh}$ , respectively [15].

## 5. Conclusions

The critical barriers in the preparation of fluid electrodes are coagulation and precipitation of zinc particles, floating zinc particles, flowing of zinc particles, and congestion of the current collector. We addressed these challenges by employing micelle technology to prepare the centrally hollow zinc microspheres and then successfully floated the zinc sols by stirring with a magnetic bar. In this study, the zinc sol was allowed to flow through a porous current collector using an electrolyte circulation system. The results showed that the electrolyte circulation system correctly regulated the internal temperature of the cell, dynamically adjusted the concentration of KOH, and removed the impurities from the electrolyte to help maintain its optimal condition. Through the use of appropriate fuel fluidity and current collection, the design and performance of zinc-air fuel cells could be enhanced.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

## Acknowledgments

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