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Practical Development of a ZnBr2 Flow Battery with a Fluidized Bed Anode Zinc-Electrode

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Energy storage is critically important to enable balancing power generation and consumption, especially in the context of renewable energy innovation, such as promoting energy distribution and management. Renewable energy sources rely on intermittent phenomena (wind, solar, etc.), which makes it difficult to predict and regulate the output to fit in with demand. The different types of energy storage systems being developed for various energy sources are solid state batteries, flow batteries, compressed air energy storage, thermal energy storage (e.g. batteries, redox flow batteries, hydrogen fuel cells, and Metal-air batteries, solar fuels), and Thermal Energy Storage (e.g. pumped hydro, compressed air, flywheel), Chemical Energy Storage (e.g. batteries, redox flow batteries, hydrogen fuel cells and metal-air batteries, solar fuel), and Thermal Energy Storage (e.g. sensible heat storage, latent heat storage, thermal chemical heat storage).

However, zinc-bromine redox flow batteries (ZnBr2), among other alternatives mentioned for storing energy are recommended and reliable to use for storing energy from renewable energy sources; such as wind and solar because of their significant benefits above conventional technologies. These include high energy densities, low costs, high efficiencies and power rating, long life cycles of more than 2000 sequences and, the capacity to operate these batteries with different applications in a wide range of various environments, etc. Regardless of all these benefits, dendritic growth during cycling in ZnBr2 cells is the main limitation of zinc-bromine batteries because it does not only lead to perforation of the membrane but can short-circuit the cell and enhances hydrogen evolution and electrode passivation. Dendrites formation normally occur during charge when zinc is reduced onto the cell electrode surface and stay longer on these electrodes more than the expected time before they are re-oxidized back into the solution. This process thus causes the deterioration of the electrode and make the battery cell to decay, short circuit the cell, reduce these cells life span, and damage them.

In order to solve these problems, the explored experimental works in this study using ANSYS for modelling the hydrodynamic flow rate and validating the results with the laboratory hydrodynamic experiment and also using COMSOL to study the potential difference between the electrodes, the potential difference etc. was carried out. Since optimizing zinc-bromine batteries cells are important to correct these problems, zinc ions deposition were impinged onto the electrode surface that cause deterioration and mechanical abrasion for these cells. As a result of this, it is necessary to improve the performance and the uptake of ZnBr2 cells systems for utility-scales electrical storage system by introducing fluidized bed zinc electrodes to these cells anode-sides as the only electroplating devices that could prevent dendrites formation.

In this paper, both the numerically modelled and experimented fluidized bed electrode presented here has the capacity to accommodate the incorporated carbon particles which were charged and plated separately on the three investigated three different electrodes feeders’ materials (carbon vs carbon), (nickel vs carbon) and (nickel vs titanium). The zinc electrode used was designed to have high surface area with no solid surface, when compared to some electrodes from other literatures. From this study, conclusions drawn highlight the novelties of the proposed method, the peculiarities of the models applied and the efficiency output of the developed battery.

Fluidized Bed Zinc-Reactors (Electrodes)

Several fluidized bed reactors are currently in use for multiple applications in chemical and engineering industries; such as a sprouted fluidized bed reactor of the literature by, like that of continuous stirred tanks fluidized bed reactors, tubular loop reactors, fluidized bed reactors, circulating fluidized bed reactors, transport fluidized beds reactors, and fluidized bed zinc electrodes as other types widely in use for different electroplating purposes within batteries cells. Mostly, and according to, zinc half-cell of zinc-bromine batteries cells behave hugely like an electroplating system for improving zinc-electrodes. Furthermore, zinc-electrodes have been examined in rechargeable zinc-air batteries of an outer frame and a porous foam electrode of supporting structures; to address the formation of zinc dendrites on external surfaces. The outer casing has a pathway where the electrolyte circulates to the treated zinc coated porous foam.
Ordinarily, cationic zinc comes out during the charging process from the aqueous solution to electroplate zinc onto negative sides of bipolar electrodes in a ZnBr₂ battery cell.

**ZBB overall battery cell reaction.**—A fully charged zinc bromide cell overall chemical reaction involves zinc reduction and bromine evolution as shown below in Equation 1:

\[ \text{ZnBr}_2 \rightarrow \text{Zn} + \text{Br}_2 \]  

Similarly, ZnBr₂ is formed from the combination of zinc and bromine during discharging of the battery as shown below in Equations 2: Reaction of zinc and bromine electrochemically during discharge to generate electricity and reform the zinc-bromide solution

\[ \text{Zn} + \text{Br}_2 \rightarrow \text{ZnBr}_2 \]  

Theoretically, the electrochemical potential of an individual zinc-bromine battery cell reaction should be 1.828 volts according to.47 Under zero current flow, this value is the Nernstian potential. Meanwhile, based on findings and observations, the presence of internal efficiencies and different resistance seen and contributed in practice are scheduled to result in slightly lower cell voltages values. The current density of a cell is another essential performance metric for a zinc-bromine battery cell system.48 Current density as measured in amperes is the value of power moving across the surface area of a cell electrode.49

However, a current density is not only limited to zinc-bromine batteries cells but has a direct influence on the capacity of electrodes in a battery cell. Regarding the energy per unit area of the battery cell and including the operating efficiency of the system overall,50,51 Furthermore, Quaternary ammonium bromides (QBr) are stored safely and considered as a separate liquid phase52 as displayed in the equation below 2. Bromide anions are converted during charging to bromine which is subsequently complexed. See Equation 3 for Bromide formation due to gain of electron and Equations 4 for Bromide reaction with quaternary ammonium bromides,53

\[ 2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^- \]  
\[ \text{QBr} + \text{Br}_2 \rightarrow \text{QBr}_3 \]

conducted a similar experimental work related to,54 and 55 by producing quaternary ammonium compounds through selecting anion during the reaction of a trialkylamine with an alkyl bromide to form a quaternary tetaalkylammonium bromide salt. Furthermore, the quaternary tetaalkylammonium bromide salt was converted to a quaternary tetaalkylammonium hydrogen salt via an ion-exchange resin by converting the quaternary tetaalkylammonium hydrogen salt to quaternary tetaalkylammonium salt of the selected anion.56–58

**Experimental Work and Approaches.**

The explored experimental work in this paper were carried out by these four approaches (1), ANSYS Fluent (2), COMSOL (3) Hydrodynamic experiments and (4), Extensive laboratory experiments: cyclic voltammetry (CV), chronopotentiometry, scanning of electrons microscopy and electrochemical impedances microscopy (EIS). According to previous studies, and the shape and size of this research work fabricated anode-reactor, a minimum fluidization velocity of 

\[ \text{0.001} \text{m/s} \]  

was accomplished theoretically by integrating some parameters into the Carman-Kozeny equation. These values include a separate void fraction values for our packed glass beads and carbon particles before charge, particles diameter in between (254 microns to 354 microns), water density of \(\text{1000 k}^3/\text{m}^3\), a zinc density of \(\text{7140 k}^3/\text{m}^3\), after charge and a glass beads density of \(\text{2520 k}^3/\text{m}^3\) from literature etc. The theoretical minimum fluidization velocity of \(\text{0.001} \text{m/s} \) was further investigated in ANSYS Fluent up to \(\text{0.098} \text{m/s} \) for us to observe an excellent fluidization state before finally agreeing a minimum fluidization velocity of \(\text{0.003} \text{m/s} \) as the best homogenous bed expansion. Furthermore, a chosen flow rate of \(\text{166.7} \text{cm}^3 \text{min}^{-1} \) was gradually increased from \(\text{1cm}^3 \text{min}^{-1} \) to fluidize the investigated glass beads and carbon particles. The flow rate was approximately \(\text{0.0046} \text{m/s} \) and \(\text{0.0047} \text{m/s} \) by converting the values to cubic meter per second \(\text{m}^3/\text{s} \) and to \(\text{m/s} \) as summarized below (\(\text{0.05m} = \text{anode reactor length} \times \text{(0.05m = anode reactor breadth)} + (0.012 \text{m = anode reactor thickness}) \times 166.7 \text{cubic meter per minute} = \text{0.005m/s} \)

**ANSYS fluent + the design numerical purpose.**—This section examines the flow of electrolyte through a packed bed of glass beads and by some added carbon particles for results validation under a minimum fluidization condition within a fluidized bed zinc-electrode that was incorporated to the anode-side of a fabricated zinc-bromine battery cell system. To determine the flow regime required to provide good fluidization. A reactor geometry was designed for the cell anode-side as presented in Figures 1a and 1b. The anode-reactor was where both the carbon particles and glass beads were separately investigated. The designed anode-reactor was now used to carry out the modelling work and to study the fluidization of particles within the half cell. Therefore, this required setting up the boundary conditions to the model, including the physical boundaries of the cells that was achieved by producing a solidwork model of the cell. This was then imported into ANSYS Fluent and for fluidization studies. It was necessary to carry out a fluidization experiment within the designed fluidized bed reactor at the cell anode-side to observe the electroplating behavior of the added carbon particles. This is in form of a parallel projection, in which all the projection lines are orthogonal to the projection plane.

**Problem description in ANSYS fluent and boundary and initial conditions.**—The fluent version in ANSYS 17.2 was used for the modelling and simulation. The fluidized bed zinc-electrode was modelled by using the dense discrete phase model (DDPM) and discrete element method (DEM) approach in ANSYS. These models are widely used for the simulation of powder systems and suitable to determine complex phenomena based on flowing particles. Dense discrete phase model (DDPM) is suitable to model dense particulate flows and accounts for particles blockages and their effect on the primary phase.59–61

The anode-side and cathode-side electrodes of this research work were both designed to suite the required standard by considering their thickness due to the impact and importance of what these developed reactors (electrodes) will provide regarding their electrolyte feeding mode and performances of the flow rate as reported in works of literature especially on redox flow batteries (RFB).62 Besides, the electrode can be modified in agreement to some works of literature by adjusting electrodes of some fluidized bed reactors with their performances. In addition, the electrodes of this research work are specially made because of their contribution to cell voltage loss during charge transfer and ohmic resistances as reported again in some pieces of literature.63,64

![Figure 1. (a) The Designed Anode-Side Reactor and (b) The Zinc Bromine Battery Cell (ZBB) incorporated with all the components (Anode & Cathode Reactor, Gaskets, Membrane and the two Anode and Cathode Electrode Electrodes.](image-url)
The anode-side reactor was initially modelled and simulated with some amount of added glass beads and was later modelled separately with graphite particles in ANSYS as a 3D fluidized bed zinc-electrode. Investigated velocity were between 0.001m/s to 0.098m/s for the glass beads and zinc-particles. The bubbling fluidized bed zinc-electrode was modelled and simulated in ANSYS Fluent by using these approaches (Huilin-Gidaspow, Schiller-Naumann, Wen-Yu, and Syamlal-Obrien model and finally selected the Wen-Yu model. The values for the initial and boundary conditions presented in Table I were fed into the system.

The injected carbon particles were tracked with the electrolyte at a flow time step of (0.0002) and for the carbon particles time step size(s). To define many injections and differentiate between them during the modelling of the fluidized bed, some procedures were introduced for describing the injection of these particles so that no problems will be encountered during the modelling and simulation as it is in most industrial applications. The modelling and simulation conducted in this research work to examine injected particles can also be used as another kind of measurement in particle systems due to science development which enables researchers to have deep insight in particle system so that the detailed behavior of the particles can be obtained.

The use of a unified Eulerian coordinate method was introduced to the computational fluid dynamics and multiphase numerical simulation of this research work to prevent and resolve any occurring flow discontinuities.

**Table II. Theoretical and Experimental Results.**

| Parameters                  | Minimum Fluidization (Umf) | Change in Pressure ΔP (Pascal) |
|----------------------------|----------------------------|--------------------------------|
| Glass Beads + Water Theory | 0.001 m/s                  | Not Calculated                 |
| ANSYS                      | 0.003 m/s                  | 0.0995218                      |
| Experiment                 | 0.0046 m/s                 | Not Measured                   |
| Carbon Particles + Water   |                            |                                |
| Minimum Fluidization (Umf) | 0.001 m/s                  | Not Calculated                 |
| Theory                     |                            |                                |
| ANSYS                      | 0.003 m/s                  | 0.07493255                     |
| Experiment                 | 0.0047 m/s                 | Not Measured                   |

**ANSYS fluent results validation - Carbon and glass beads.—** Figure 2 is the fluidized bed zinc electrode schematic diagram. The validated results presented in Table II were explored experimentally, numerically and theoretically. These include the minimum fluidization velocity (Umf) and the pressure drop of the investigated added glass beads and carbon particles with water within the anode reactor. However, the pressure drop was not explored theoretically and during the laboratory experiment but only numerically in ANSYS. Theoretically, the minimum fluidization velocity was in good agreement with the ANSYS numerical value. Experimentally, theoretically and numerically, a lesser flow resistance was observed within the anode-reactor when added with glass beads compared to the carbon particles. This was due to the similarities between their densities and mass.

Based on the shape of our fabricated anode-reactor and previous literatures, a minimum fluidization velocity of (0.001m/s) was accomplished theoretically by integrating some parameters within the Carman-Kozeny equation. These values include a separate void fraction values for our packed glass beads and carbon particles before charge, particles diameter in between (254 microns to 354 microns), water density of (1000 kg/m³), a zinc density of (7140 kg/m³), after charge and a glass beads density of (2520 kg/m³) from literature etc. The theoretical minimum fluidization velocity (0.001 m/s) was further investigated in ANSYS Fluent up to 0.098 m/s for us to observe an excellent fluidization state before finally agreeing a minimum fluidization velocity of (0.003 m/s) as the best homogenous bed expansion.

**Table I. Boundary and Initial Condition.**

| ANSYS FLUENT DDPM + DEM MODEL |
|-----------------------------|
| Names                       | Glass Beads               | Zinc Particles              |
| Primary Phase               | Liquid                    | Liquid                      |
| Secondary Phase             | Solid Density (2520 kg/m³) | Solid density (7140 kg/m³)  |
| Mesh Type                   | Multizone                 | Multizone                   |
| Inlet Liquid Temperature    | 293 K                     | 293 K                       |
| Inlet Pressure              | 101325 Pascals            | 101325 Pascals              |
| Outlet Pressure             | 101600 Pascals            | 101600 Pascals              |
| Inlet Velocity Magnitude    | 0.003 m/s                 | 0.003 m/s                   |
| Total Flow Rate             | 0.00408 (Kg/s)            | 0.00038 (Kg/s)              |
| Minimum Particle Sizes      | 0.00038 (m)               | 0.00042 (m)                 |
| Maximum Particle Sizes      | 0.00042 (m)               | 0.00042 (m)                 |
| Physical Model              | Wen-Yu                    | Wen-Yu                      |
| Particle Time-Step Size     | 0.002                      | 0.0002                      |
| Particles travel velocity   | 0-50 m/s                  | 0-50 m/s                    |
A chosen flow rate of 166.7 cm$^3$ min$^{-1}$ was gradually increased from 1 cm$^3$ min$^{-1}$ to fluidize the investigated glass beads and carbon particles. The flow rate was approximately 0.0046 m/s and 0.0047 m/s by converting the values to cubic meter per second m$^3$/s from 1 cm$^3$/min. The flow rate was approximately 0.0046 m/s and 0.0047 m/s as summarized below (0.05 m = anode reactor length) $\ast$ (0.05 m = anode reactor breadth) $\ast$ (0.012 m = anode reactor thickness) $\ast$ 166.7 cubic meter per minute $= 0.005$m/s.

Discussion on glass beads and carbon.—The designed reactor during the modelling and simulation showed that it has capability of producing an electrode that reduces losses during charging and discharging and can create enough mass transport of zinc ions and capable of quick exchanging of electrons based on the speed of charging and discharging onto plane surfaces according to the observations made in ANSYS CFD Fluent. Numerically, both the experimented (a) glass beads and (b) graphite particle residence time (mixture) seconds are displayed in Figures 3a and 3b. The simulation time of the experimented glass beads was for a short period to prevent the particles from escaping from the anode-reactor’s outlet compare to the added zinc-particles.

The added glass beads were not uniformed within the reactor unlike the zinc-particles during the numerical simulation. These two particles densities carbon and glass beads could have resulted to such discrepancy. For instances, the glass beads density was (2520 kg/m$^3$) and the zinc particles solid density was (7140 kg/m$^3$). Furthermore, these has affected the spherical shapes of these two investigated particles which have also contributed to the outcome of the result. Specifying different parameters had assisted through the numerical simulation and the used of rosin-rammler particles distribution in setting the injection properties in Fluent as an addition to the initial applied velocity at the zinc-bromine battery cell’s anode inlet, temperature and total flow rate.

COMSOL.—Dendrite clusters, porous electrode media, or 2 phase bromine phenomena have not been presented in COMSOL due to the due the research license that was available. Therefore, not all models were accessible during the numerical modelling experiment. Furthermore, both the anode and cathode electrode (reactors) were designed to be thin for a more proper conductivity because one of the most important aspects in the design of electrochemical cells is the current density distributions in the electrolyte and electrodes as non-uniform current density distributions can be detrimental for the operation of electrochemical processes. In many cases the parts of an electrode that are subjected to high current density degrade at a faster rate. Knowledge of the current density distribution is also desired to optimize the utilization of the electrocatalysts, because these are often made of expensive noble metals. Non-uniform deposition and consumption, as well as unnecessarily high overvoltages, with resulting energy losses and possibly unwanted side-reactions, may be other effects that one would like to minimize.

Three key stages were involved during the computational experiment

1. The vigorous mixing of the electrolyte, the ionic migration was the dominating transport mechanism and the general mass balance in the electrolyte, since it was a steady-state conditions and that no homogeneous reactions occur. These processes were governed by the following Equations 5 and 6

$$\nabla \cdot \mathbf{N} = 0 \quad \text{[5]}$$

where $\mathbf{N}$ is the flux of species $i$ (SI unit: mol·m$^{-2}$s), which in turn is governed by:

$$D_i \nabla c_i - z_i m_i F \nabla \phi + c_i u = N_i \quad \text{[6]}$$

where $c_i$ represents the concentration of the ion $i$ (SI unit: mol/m$^3$), $z_i$ its valence, $D_i$ its diffusivity (SI unit: m$^2$/s), $m_i$ its mobility (SI unit: mol·m$^{-2}$s·V$^{-1}$), $F$ denotes the Faraday constant (SI unit: As/mol), the ionic potential, and $u$ the velocity vector (SI unit: m/s).

2. The kinetics at the electrode.

3. Mass transportation of ion through diffusion, convection, and migration.

Furthermore, to reduce the experiment computational times in COMSOL, the cell behavior was simulated in a 2-D dimension by cutting the cross section and making them to be perpendicularly through each of the layers. By modelling the cell system can be used to reduce the required time of the experiment via programming some values on COMSOL because it will point out the independent and experimental designed parameters and how they can be modified to better the performance of the model.

To help design the laboratory experiments described in this paper, it was necessary to model the electrochemical behavior of the cell during charge, discharge in three key states: (i) almost fully charge, (ii) mid-charge and (iii) almost fully discharge, in order to predict the current generated, potential differences between the electrodes, the current vs voltage response, and the changes in concentrations of key electrolyte composition. In this section, a two-dimensional (2D)
model) ZnBr$_2$ model geometry was used and consists of five different layers as shown in Figure 4.

This includes (a) the anode feeder electrode (b) anode-side reactor (b) Nafion ion-exchange membrane, (c) cathode-side reactor and (e) cathode feeder electrode. The anode and cathode feeder electrodes provide the electrical connection externally to the system. The Nafion membrane separates the two-electrolytes from mixing together. The anode-side reactor is injected with un-measured added zinc particles. The composition of the anode-side and cathode-side electrolytes are given in Table III. The system was simulated using COMOL Multiphysics 5.3a and no additional program modules.

Anode zinc concentration.—Not all the concentrations results fed into the system at the cell anode-side were discussed in this section; since the area of interest focusses on zinc depleted, bromine formed and the amount of bromide concentration at the cell anode-side and cathode-side. Therefore, only the added zinc concentrations results were mentioned in this section. The anode zinc-electrode zinc concentrations were (2.5M), before charge, at a current rate in between $-0.1\,\text{A}$ and $0.1\,\text{A}$ and was (3.25M) for the mid-charged and (4M) for the discharged. The discharge current rate was also in between $-0.1\,\text{A}$ and $0.1\,\text{A}$. At $-0.1\,\text{A}$ and $0.1\,\text{A}$ as the mid-charge, more zinc was used at charge, by depleting from (2.5 mol to 2.41 mol) than at a current rate of $-0.1\,\text{A}$ (2.4 mol and 2.32 mol). According to Figures 5bi and 5bii, the depleted zinc during mid-charge was (3.25 mol and 3.16 mol) at $0.1\,\text{A}$ and between (3.1 mol and 3.07 mol) at $-0.1\,\text{A}$. In Figures 5ci and 5cii, it was between 4 mol and 3.9 mol, while at $0.1\,\text{A}$; and it was between 3.9 mol and 3.82 mol, while at $-0.1\,\text{A}$ for the discharge. These predictions were all in good agreement with the laboratory experimental work.

Cathode bromide concentration.—The programmed bromide (Br) concentration for the charge was 0.01M, and 1.5M for the mid-charge and 3M for discharge. The same bromide concentration was formed at charge (0.01 mol to 93.718 mol at $0.1\,\text{A}$) and at $-0.1\,\text{A}$ it was (114,542 mol and 208.25 mol). For the mid-charge, it was also increased by 0.08 mol (1.5 mol and 1.58 mol at $0.1\,\text{A}$) and by 0.09 mol (1.59 mol and 1.68 mol at $-0.1\,\text{A}$). It was (3.01 mol and 3.09 mol) at $0.1\,\text{A}$ and (3.11 mol and 3.2 mol) at $-0.1\,\text{A}$ for the discharge. The bromide concentration during the real experiment might have varied due to experimental conditions.

### Table III. Charged, Mid-charged and Discharged Concentrations.

| ANOLYTE COMPOSITION | ANOLYTE COMPOSITION |
|---------------------|---------------------|
| **Elements** | **Charge** | **Mid-Charge** | **Discharge** |
| Zinc (Zn$^{2+}$) | 2.5M | 3.25M | 4M |
| Bromide (Br$^-$) | 6M | 6M | 6M |
| Chlorine (Cl$^-$) | 3M | 3M | 3M |
| Potassium (K$^+$) | 1M | 1M | 1M |
| Hydrogen (H$^+$) | 0.00316M | 0.00316M | 0.00316M |
| Water (H$_2$O) | 55.555M | 55.555M | 55.555M |

| CATHOLYTE COMPOSITION | CATHOLYTE COMPOSITION |
|-----------------------|-----------------------|
| **Elements** | **Charge** | **Mid-Charge** | **Discharge** |
| Bromide (Br$^-$) | 0.01M | 1.5M | 3M |
| Chlorine (Cl$^-$) | 1M | 1M | 1M |
| Potassium (K$^+$) | 4M | 1M | 4M |
| Bromine (Br$_2$) | 1.5M | 0.75M | 0.01M |
| Water (H$_2$O) | 55.555M | 55.555M | 55.555M |
Figure 5. Cell Model Electrolyte Potential and Current Vs Voltage (a) Charged at 0.1A & −0.1A (b) Mid-Charged at 0.1A & −0.1A and (c) Discharged at 0.1A & −0.1A.
have increased during the laboratory experiment. Numerically, the model has showed that the original ZnBr2 solution can be reformulated during discharge. The simulation outcomes showed that the numerical modelling and experimental data were compatible and in good agreement.

**Cathode bromine concentration.**—The bromine (Br₂) concentration for the charge was 1.5M, and 0.75M for the mid-charge and 0.01M for discharge. The model predicted a change to the discharge concentrations (0.01M). More bromine was formed during charge by 0.09M. Both the mid-charge and discharge concentrations elevated separately by 0.094M. At the cell cathode-side, the model has showed that more bromine will be formed during charge. During charge the concentration was between (0.16 mol to 1.4 mol at 0.1A) and (1.7 mol and 3.17 mol at −0.1A). For the mid-charge it was (84.3 mol and 753.1 mol at 0.1A) and (920 mol and 1672.7 mol at 0.1A). And (10.4 mol and 93.8 mol at 0.1A) and (114.6 mol and 208.4 mol at −0.1A) for the discharge.

**COMSOL: results description + discussion.**—Electrolyte potential vs current and voltage. —The predicted electrolyte potential and current versus time by the model are presented in Figures 5ai to 5ci. These predicted results are for the charge state, partially charged state and discharge state. The electrolyte potentials presented in Figures 5ai to 5cii were observed after running the model under a set of operating condition at a steady state. Mathematically, the model was computerized under a constant temperature of 293.15 (K) with current flowing in the ZnBr2 cell. The cell was set to first charge at a current rate of 0.1A and −0.1A and discharged at 0.1A after charging at 0.1A at the same time. The mid-charge was programmed up at 0.1A and −0.1A for the cell to store energy and to predict the cell electrolyte potential when partially charged. The red mapped color on the modelled geometry at the anode zinc-electrode identifies charged zinc.

The model predicted the expected electrolyte potentials for the charged, mid-charged and discharge. These values corresponded with the modelled geometry at the anode zinc-electrode identifies charged trolyte potential when partially charged. The red mapped color on the modelled geometry at the anode zinc-electrode identifies charged zinc.

Flowing of electrons were identified by the black arrows within the anode reactor apart from the carbon particles before increasing from 1 cm³ min⁻¹. This flow rate was approximately 0.0046 m/s and 0.0047 m/s by converting the values to cubic meter per second m³/s and to m/s as summarized shown: 0.05m+0.05m+0.012m+166.7 cubic meter per minute = 0.005m/s. The apparatus (test tube flowmeter and fluidized bed anode-reactor) used for this experiment were carefully checked to know their condition or else they might affect the experimental data.

1. The carbon particles were filled within the anode-reactor up to a height of 35 mm and examined. The same height applies to the added and examined glass beads. However, only the carbon-particles were between 254 microns to 354 microns, as presented in Figure 7c.
2. The graphite particles density was 7140 kg/m³ and the glass beads particles density was not measured but appeared very tiny compared to the carbon particles, as presented in Figure 7d.

**Hydrodynamic results and discussion.**—Recurrently, high internal resistances were encountered within the fabricated zinc-bromide cell throughout the experimental work. From the anode electrode to the cathode electrode, the frequency was high but reduced toward the cathode electrode, as presented in Figures 6a to 6c. The first impedances demonstrated 4Ω from the cell anode-side. The problem has made the charge and energy efficiency to be low compared to most of the results conducted in other articles. For instance, with the second feeder current collectors, the carbon and nickel feeder electrode at 3-cycles of charge and discharge, established a maximum charge and energy efficiency of CE of (47.5%, 64.5% and 63.3%) and energy efficiency, EE of (13.97%, 18.9% and 18.6%) at a current rate of 0.1A and 0.1A. The size of the fabricated and incorporated two reactors (anode and cathode) could have contributed the discrepancy in the results. Subsequently, this has instigated making the shape of the reactors to be thin when modelled in 2D on COMSOL so that these electrodes will be conductive. However, both the added glass beads and injected carbon particles fluidized as expected and behave in the state of the fluid, as presented in Figures 7c and 7d. At 0.0046 m/s, the glass beads had gained its steady state and at 0.0047 m/s, the investigated carbon particles had also gained its steady state.

**Laboratory experimental condition.**—Carbon-anode vs carbon-cathode.—Carbon offers access to a wide anodic potential range, low electrical resistance, low residual current, and a reproducible structure of the electrode surface. Few results out of all the explored chronopotentiometry experiment are presented here in this paper with their energy and charge efficiency for the first set feeder electrodes materials (carbon-anode and carbon-cathode). Exploring various electrochemical measurements using different current rates and techniques has allowed to know the most conductive electrode materials that can be recommended in future to fabricated ZBB cells through these introduced electrochemical measurement methodologies: cyclic voltammetry (CV), chronopotentiometry, impedances and taking some minimum fluidization (0.001 m/s) that were both separately investigated in the anode-reactor. In this equation, \( \varepsilon_{mf} \) is identified as the function of the shape and distribution of the particles size (\( d_f^2 \)) is the diameter, \( \rho_f \) is the density of the particles and \( \rho \) as the density of water.

\[
1.75 \frac{\rho_f}{D_p \varepsilon_{mf}^2} u_0 + \frac{150 (1 - \varepsilon_f)}{D_p \varepsilon_{mf}^2} u_0 + (-g \rho_f) = 0 \quad [7]
\]
scanning of electrons microscopy. All the explored cyclic voltammetry’s were at 25mV/sec at 1 cycle after charging and discharging current stored by the fabricated zinc-bromine battery cell at the various programmed rates. The cell impedances will later be discussed somewhere in this paper with the outcome of the scanning of electrons microscopy (SEM). The explored charged and discharged experiment at various current rates with the first set electrode feeder materials, carbon vs carbon, was coupled with 3M of KBr (535.51g), 1M of KCl (111.89g) as the cathode-side electrolyte and 3M of ZnBr₂ (675g), 1M of ZnCl₂ (205g), and 1M of KCl (111.826g) as the anode electrolyte solution.

1st feeder electrode results and discussion.—Chronopotentiometry @ (0.1A & −0.1A) @ (3600 secs & 500 secs).—In Figure 8c(aii), only the cell charge efficiency was calculated, but very low compare to the charge efficiency of the experimental result in Figure 8c(aii). The cell showed a negative potential of 1.1V and a charge voltage of 2V. The cell completed its charged and discharged at the actual programmed current rates (0.1A, and −0.1A) and within 3600 seconds and 500 seconds but with a strange voltage. During charge the cell watt was 0.2 Watt.Hr (0.0002 Kilowatt.Hr) and 0.11 Watt.Hr (0.0001 Kilowatt.Hr) during discharge. The cell stored 360C at 3600 seconds and discharged the stored current at the expected 500 seconds.

Carrying out a deep discharge on the cell at a current rate of 0.1A and −0.1A can stress the battery cell if a partial discharge (500 secs) on the cell can result to a negative voltage. Furthermore, this could have affected the cell energy efficiencies (CE and EE). Therefore, it is not advisable to partially or completely discharge current stored by the cell rather than programming the cell to store more current and programming the cell to discharge at a proper discharge time and currents. The cell was able to reverse back its polarity after it was fully discharged. This was confirmed via other chronopotentiometry measurements that was later carried out on the cell which indicated that the cell was not damaged and required no replacement.
Figure 7. (a) Investigated Glass Beads (b) Anode Zin-Electrode Anode Reactor with (c) Fluidized Glass Beads and (d) Carbon Particles.

Chronopotentiometry @ (0.2A & −0.1A) @ 1500 secs & 1300 secs.—At 2.1V from the graph plot in Figure 9a(ii), the cell energy was 0.42 watt.Hr with the following efficiencies: CE, 43.3%, and EE, 15.63%. The cell demonstrated a voltage of 1.3V at discharged. The battery cell was unable to store the expected 720C due to loss of energy and failed to discharge the programmed (−360C) of energy. The cell was fully charged at 1500 secs but could only store 300C out of the anticipated 720C. Therefore, 460C of energy was lost, and the cell still has 2300 secs to complete its charged. Additionally, the cell was able to discharge (−130C) at 1300 secs out of the expected 360C and lost (−210C).

Cyclic voltammetry @ 25mV/Sec - carbon feeder electrodes.—The cell encountered high resistance during charge. This occurrence contributed to a reduced flow of current and zinc depletion. Based on the high slope, the cyclic voltammetry shape indicated a high resistance of about 5 ohms. Applying a slow scan rate to this cyclic voltammetry experiment was to observe a fast-chemical reaction. From the graph results, the reduction voltage occurred at 1.1V and reduction current peak at −30mA. Zinc depletion (Oxidation) continued until 2.3V with the oxidation current peak was between 200mA and 300mA.

Calculations (Ai) 0.1A & −0.1A @ 3600 secs & 500 secs

1. Charge Efficiency (CE)

\[
\frac{\text{Charged Recovered (Discharge)}}{\text{Charged Input (Charge)}} \times 100\% = \frac{50}{360} \times 100\% = 13.8\%
\]

2. Energy Efficiency (EE)

\[
\frac{\text{Energy Recovered (Discharge)}}{\text{Energy Input (Charge)}} \times 100\%
\]

The energy efficiency was calculated but not recorded due to a negative discharge voltage.

The cell programmed discharge cut off voltage (0V) was exceeded. Therefore, this had resulted to the calculated negative voltage due after the cut off voltage which has made the chemistry to be different.

Calculations (Ai) 0.2A & −0.1A @ 1500 secs & 1300 secs

3. Charge Efficiency (CE)

\[
\frac{\text{Charged Recovered (Discharge)}}{\text{Charged Input (Charge)}} \times 100\% = \frac{130}{300} \times 100\% = 43.33\%
\]

4. Energy Efficiency (EE)

\[
\frac{\text{Energy Recovered (Discharge)}}{\text{Energy Input (Charge)}} \times 100\%
\]

\[
\frac{\text{Charge Recovered} \times \text{Average Voltage During Discharge}}{\text{Charge Input} \times \text{Average Voltage During Charge}} \times 100\%
\]

\[
= \frac{130 \times 0.707}{300 \times 1.96} \times 100\% = 15.63\%
\]
Recognition of Cu and cell efficiency after reversion and description of results - carbon feeder electrodes.—Batteries cells capacities can be reduced, and the resistances can be increased, when different charges conditions are passed to them. Such result can always be depending on different combination and decomposition of the active materials and chemical reactions. Therefore, this has instigated the different charges rate carried out on the experimented zinc-bromine battery cell since it has been reported in previous studies and based on the earlier charged passed on the cell in this research work. Many research studies has also confirmed how the addition of active compound, and many other elements existing in batteries cells can give rise to undesirable chemical reactions. In this section, the battery cell was charged and discharge at different acceleration voltages and programmed to charge and discharge at some different rates to observe the electrodeposited metallic zinc elements via using scanning the electron image with the SEM device (JSM-6010LA/JSM-6010LV). A charge was passed twice at this currents rate (0.1A and −0.1A) to confirm if the strange electrochemical noise was from the centrifugal pump and for further elucidation on the percentage of the efficiency that can be derived from the cell. This has made the current results in this section as three different chronopotentiometry measurements at these current rates: (0.1A, 0.1A, and 0.25A) and (−0.1A, −0.1A, and −0.25A) and three cyclic voltammetry. This is presented in Figures 10a–10d for the chronopotentiometry measurements and Figure 10e–g for the cyclic voltammetry (CV), respectively. The measured charge efficiencies for the presented chronopotentiometry results in Figure 10 were 22%, 5.71%, and 2.77%. The calculated energy efficiency was 5.90%, 2%, and 1.07%. Brown deposits identified to be copper after charging.
the battery cell, was deposited on the electroplated zinc, as shown on Figure 11. The energy efficiency and charge that was first tested, is presented in Figure 12.

**Findings and comments – carbon vs carbon feeder electrodes.**— Charged passed to the cell at those low currents rates for two case studies, might have increased the resistances or possibly the bed was not conductive as expected to fluidize and charge the added carbon particles and result to zinc electrodeposition. The parameters for case study 1 were 0.1A, 0.1A, and 0.25A and while the parameters for case study 2 were −0.1A, −0.1A, and −0.25A. The presented bar charts supported each part of the data, as presented in Figure 12 (1), (2) and (3). Furthermore, the cell temperature increased sharply without any short circuit. The charge and energy efficiencies might be reduced due to secondary reaction; like the redox reaction within the cell.

Some parameters of the battery cell need to be monitored; such as the voltage, temperature and current during passing charges. These parameters are important so that the cell can be kept in a good operating condition. Other areas that required concentration is the electrolyte depletion and preventing the cell from overcharging. The electrolyte should be change as this can be degrading slowly. This can make the voltage to fluctuate, have low coulombic efficiency in relation to the discharge capacity and charge capacity. This can lead to a non-uniformed electrodeposition of zinc like dendrite formation. However, the incorporated high surface area anode-reactor will certainly prevent dendrite problems. Brown deposit identified as copper were also observed within the cathode-side electrolyte during those explored charged passed and on the electrodeposited zinc within the anode-reactor, as shown in Figure 11. Such observed results impelled interrupting the cell from operating further and led to pulling the cell.
components apart from a proper cleaning and introducing a separation technique to sieve the cathode electrolyte solution and the anode electrolyte from these escaped zinc-particles. Fitting materials that were not chemically resistance had contributed to such deposition.

The brown deposit had converted the zinc-bromine batteries cell to a copper-zinc battery cell but was later reverted to a zinc-bromide cell of which the reverting process involved carrying out the filtration procedure repeatedly to separate these sediments from the anode and cathode electrolyte solution. The battery cell was able to establish a good redox reaction after these processes and according to the electrochemical results and from the experimental observation. However, the cell efficiencies were too low due to internal losses, and some of the energy were assumed to be converted into heat, as presented in Figure 12. The cell metallic bolts and nuts must be changed to first avoid the transferring of current onto them. The opening charge and discharging voltage was 1.3V and 1.9V for 3600 secs and 7100 secs during discharge but could discharged slightly (0.5V) at 3600 secs to 4000 secs and 200 secs to 3500 secs during discharge.

During the charged passed at a current rate of 0.25A and −0.01A at both 3600 secs, the cell stored 900C at 3600 secs and lost −1C in between 3600 secs and 7100 secs during discharge but could discharge −35C at exactly 3500 secs. The cell voltage was 1.9V during charge and 1.0V for the discharged. The cell showed 0.475Watt. Hr (0.000475 Kilowatt.Hr) for the charge and 0.014Watt. Hr (0.00014 Kilowatt.Hr) for the discharged. At exactly 3500 secs the cell could also discharge −35C of energy. Both the charge and energy efficiencies were low due to the poor performances.

As displayed in Table IV, the cell demonstrated a very detrimental voltage (4V) at a current rate of 1A and −0.05A for 3600 secs. At 0.5A and −0.01A, the cell showed a voltage of 2.6V at 7000 secs. The cell voltage was low (1.5V) at a current rate of 0.25A and −0.01A. At 0.1A and −0.05A for 3600 secs, the cell established 4V , 4Watts. Hr (0.000475 Kilowatt.Hr) during charge and 1.3V, 0.065Watt. Hr (0.000065Kilowatt.Hr) during discharged. The lost current was 5C out of 175C instead of 180C. The discharged current accumulated within (7100 secs) to (3600 secs). The charge passed during charge was 3600C and none of the charge passed throughout the charge period was recorded.

**Table IV. Experimental Data’s of the investigated two-carbon materials with 3M of KBr (535.51g), 1M of KCl (111.89g) as the cathode-side electrolyte and 3M of ZnBr2 (675g), 1M of ZnCl2 (205g), and 1M of KCl (111.826g) as the anode electrolyte solution.**

| Current Rates | Charge Efficiencies | Energy Efficiencies |
|---------------|---------------------|---------------------|
| 0.25A Vs −0.25A | 11.1% | 5.48% |
| 0.1A Vs −0.005A | 4.86% | 2.94% |
| 0.25A Vs −0.01A | 3.88% | 1.81% |
| 0.5A Vs −0.01A | 1.94% | 1.25% |
| 1A Vs −0.05A | 4.86% | 2.21% |

**Five cycles of chronopotentiometry - carbon feeder electrodes.**— As mentioned earlier in Section 3.12, to compare the cell energy efficiencies, the cell was further charged at these current rates of 0.25A, 0.1A, 0.25A, 0.5A and 1A, and discharges at −0.25A, −0.005A, −0.01A, −0.01 and −0.05A, carried out under different set times in seconds. The cathode electrolyte solution contains 3M of potassium bromide (KBr) (535.51g) and 1M of potassium chloride (KCl) (111.89g). The anode-side electrolyte also includes the following chemicals solution: 3M of zinc-bromide (ZnBr2) (675g), Solution, 1M of zinc chloride (ZnCl2) (205g), and 1M of potassium chloride (KCl) (111.826g). The anode electrolyte density was 1.47gcm⁻³.

**Description of results - carbon feeder electrodes.**—Figures 13 and 14 are the charge results plots and bar chart. By charging the battery cell at those current rates stated in this section 3.13.1 was to observe which of the current rates that can rapidly make the battery cell to have a better charge and energy efficiency of approximately 90% compared the previous results. The charged passed at 0.25A for 3600 secs and −0.25A for 400 secs has made the battery cell to stored 900C at 3600 secs during charge but lost (−700C) in between 3600 secs to 4000 secs and only stored 100C at 400 secs from the charge passed to discharge. The charged voltage was 1.9V with 0.475Watt. Hr (0.000475 Kilowatt.Hr) and 0.5V as the discharged with 0.125Watt. Hr (0.000125 Kilowatt. Hr). In between (0.1A and −0.005A), at 3600 secs to 7100 secs, the stored current from the charged passed was −17.5C instead of −18C and 360C for the charged at exactly 3600 secs. The lost charge passed during discharge was −0.5C. The cell voltage was 1.5V during charge with 0.15Watt. Hr (0.00015Kilowatt. Hr). The discharged voltage was 0.7V and demonstrated 0.0035Watt. Hr (0.000035Kilowatt. Hr.).

## Findings and comments – carbon vs carbon feeder electrodes.—

As displayed in Table IV, the cell demonstrated a very detrimental voltage (4V) at a current rate of 1A and −0.05A and 7000 secs. At 0.5A and −0.01A, the cell showed a voltage of 2.6V at 7000 secs. The cell voltage was low (1.5V) at a current rate of 0.25A and −0.01A. At

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**Figure 11.** Brown deposits identified to be copper after charging the battery cell.

**Figure 12.** Charge-(Blue) and Energy-(Orange) Efficiencies a current rate of (1) 0.1A and −0.1A for 3600 secs and 800 secs (2) At 0.1A and −0.1A for 3500 secs and 200 secs (3) 0.25A for 3600 secs and −0.25A for 100 secs of 3M of KBr (535.51g), 1M of KCl (111.89g) of cathode electrolyte solution and 3M of ZnBr2 (675g), 1M of ZnCl2 (205g), and 1M of KCl (111.826g) of anode electrolyte solution.
Figure 13. Charge and Discharge: 3M of KBr (535.51g), 1M of KCl (111.89g) of cathode electrolyte solution and 3M of ZnBr₂ (675g), 1M of ZnCl₂ (205g), and 1M of KCl (111.826g) of anode electrolyte solution at (a) 0.25A for 3600 secs, −0.25A for 400 secs (First Top Left) (b) 0.1A for 3600 secs and −0.005A for 3500 secs (First Top Right) (c) 0.25A for 3600 secs, and −0.01A for 3600 secs (First Middle Left) (d) 0.5A for 3600 secs, and −0.01A for 3600 secs (First Middle Right) (e) 1A for 3600 secs, and −0.05A for 3500 secs (Bottom Centre).

0.1A and −0.005A, the cell voltage was 2V. The cell further showed a very low voltage at a current rate of 0.25A and −0.25A. The cell demonstrated and had a good redox reaction during the charge state and according to the graph results, but the materials were not electrically conductive as expected. It was assumed that the entire cell energy efficiency had been affected due to the problem. The membrane can be re-boiled to be more conductive and the pH level of the two-electrolytes should be frequently checked since they determine the number of protons at the battery cell anode-side. Flow batteries cell electrolytes must not be ionically conductive alone to have higher efficiency, but also to be chemically stable, be conductive under a wide range of conditions, and be good mechanically. The anode electrode feeder must be changed to a better material that can be more conductive. Different Coulombs of charge were lost by charging the cell at different current rates and discharges rates. The battery cell is so resistive, charging it at high current rates should be avoided but to discharge at a much lower rate. But not quite sure if the charges passed can be retrieved back from the cell at a lower current rate since the cell did not reach a point where the voltage collapsed. However, running the cell longer could have been a good idea for comparison of results.

Discussion on 1st feeder carbon feeder electrodes.—

• Unanticipated side reaction could be occurring by charging the cell at 0.1A and −0.1A instead of a current rate of 0.2A and −0.1A. Therefore, the electrodeposition of zinc is better at this current rate: 0.2A and −0.1A; as this favours the Zn reaction. Similar current rate could be repeated later to observe if the cell resistance will be reduced. The battery cell required dismantling it and cleaned to improve the
efficiency and examine it methodically to prevent any future fault. The lost current might have gone into the added zinc particles or via wiping or leakage. From the bar chart in Figure 8 (charge and discharge), the cell performed better at a current rate of 0.2A for 1500 secs and at −0.1A @ 1300 secs. The system electrochemical design required checking it. This include the zinc-electrode and cathode-electrode and the composition of the electrolyte. The high resistance on the zinc-bromide cell can also be reduced by lowering the salts concentration. Furthermore, placing the two electrodes more closely to each other and firmly can also be of help and reducing the thickness of the gasket demarcating these two electrodes for more closed intact.

- Different energy efficiencies were established by the cell through the passed charged and due to the internal losses and heat that was encountered and suffered by the cell as presented through the bar chart in Figure 14. Although these efficiencies were not good as desired; but still the best efficiency can be given to the 1st chronopotentiometry measurement at a current rate of (0.1A, −0.1A @ 3600 secs and 800 secs) because of the observed charge efficiency of 22.22%, and energy efficiency of 5.90%.

- The presented bar charts confirmed each part of the data. For instances, in Section 3.13.1, the CE efficiency was better than the EE efficiency. The cell demonstrated different results that cannot be presented due to the following indicated energy efficiencies: 11.1% as the 1st CE efficiency, 4.86% as the 2nd CE efficiency, 3.88% for the 3rd CE efficiency, 1.94% for the 4th CE efficiency and 4.86% for the 5th CE efficiency. These observed results showed that the charge that was passed into the cell system were not completely recovered and none of these experiments can be recommended as a good zinc-bromine battery. The result also showed that almost 88.9% of the efficiency were lost, which was due to the physics within the cell walls in the experimental set-up.

**Carbon vs nickel and Titanium vs nickel.**—Nickel (Ni) is a good corrosion resistant choice for electrode feeders but may still have problems in halide conditions. Titanium is a non-ferrous metal with excellent corrosion resistance, good fatigue properties, and a high strength-to-weight ratio. Titanium’s excellent corrosion properties result in the use of titanium for electrochemical processes such as electropolishing, electrophoresis, electrodeposition, electroforming, electro-hydrolysis, electro chlorination, electrofluorination, and electrolysis. Titanium has the highest strength to weight ratio of any metal and even in its unalloyed form it is as strong as some steels but around 45% lighter and has a high melting point. Titanium alloys contain additional quantities of other elements such as vanadium and aluminum to further enhance mechanical properties and corrosion resistance.

As described in Description of results—carbon feeder electrodes section, the cell was later programmed to charge and discharge with the 2nd set of electrodes (nickel and carbon electrode) and the 3rd set of electrodes (nickel and titanium electrodes) to be sensitive to these materials. These electrodes are to indicate the excellent conductors of electricity and were compared to the 1st feeder materials of these electrodes; carbon-anode and carbon-cathode, as shown in Figures 15a and 15b. However, only the best explored experimental readings are presented for these two, and three sets electrodes feeder materials at (a) Carbon and Nickel at a current rate of 0.1A and −0.1A for (1), for (4000 secs and 1900 secs), and (2), for (3100 secs and 2000 secs), and (3) for (3000 secs and 1900 secs). (b) 3-Cycles of Charged and Discharge at a Current Rate of 0.1A and −0.1A for (1800 secs and 900 secs), (1810 secs and 900 secs), and (1705 secs and 900 secs) via using the Nickel Vs Titanium with 3M of KBr (535.51g), 1M of KCl (111.89g) as the cathode-side electrolyte and 3M of ZnBr2 (675g), 1M of ZnCl2 (205g), and 1M of KCl (111.826g) of anode electrolyte solution (c) Cyclic voltammetry at 25mVs taken after investigating the Nickel and Titanium Electrode.

**Description and analysis of results.**—Carbon vs nickel.—As showed in Figure 16a, less passed charge was recovered back (310C) in between (5900secs to 9000secs) during the 2nd cycle instead of having 360C. The lost charge passed was 50C. But during the discharge, 200C in between (900 secs to 1100 secs) was retrieved as 180C was expected. Charged passed during the 3rd cycle was 300C in between 1100 secs to 14200secs instead of 360C. The lost charged was 60C during charge and gained 10C in between 143000 secs to 162000 secs from the charge passed. However, the expected Coulombs from the charge passed was 180C. The charged passed increased by 40C during the 1st cycle of charge in between 3600 secs to 4000 secs and during discharged by an additional 10C in between 4000 secs to 5900 secs. The cell demonstrated 1.8V during charge and 0.4V during discharged throughout the passed charge for the charge and discharge.

The battery cell was able to complete the three cycles of charges and discharges at the exact programmed time and at a current rate of (0.1A, −0.1A). The carbon and nickel current collectors showed a large reduction process during the forward scan and a peak during the reverse scan from a voltage of 2.4V to 1.6V, as shown in Figures 16a and 16b. The cell abnormal performance was due to the added sequestering agent (Tetrabutylammonium bromide) in the cathode-side electrolyte solution. The old cathode-electrolyte with the new anode-electrolyte was also compatible to charge the cell at 100mA for 1800 seconds but it was expected to charge up to 1000mA. The cell also discharged at these current rates (~100mA), (~200mA), and (~300mA) for 900 seconds and elevated from 1.3V to 2.2V. However, the new electrolyte solution and its reaction within the cell may not make the cell to charge. No leakage was also encountered on the cell during the experiment.

Titanium Vs nickel.—The result presented in Figures 16c–16d and Figure 17 has showed that the old electrolyte performed outstandingly. But the cell could only charge at 100mA, 200mA, and 300mA for 1800 seconds when it was expected to charge up to 1000mA. The cell also discharged at these current rates (~100mA), (~200mA), and (~300mA) for 900 seconds and elevated from 1.3V to 2.2V. However, the new electrolyte solution and its reaction within the cell may not make the cell to charge. No leakage was also encountered on the cell during the experiment.

The cell abnormal performance was due to the added sequestering agent (Tetrabutylammonium bromide) in the cathode-side electrolyte solution. The old cathode-electrolyte with the new anode-electrolyte was also compatible to charge the cell at 100mA for 1800 seconds and discharge at a current rate of ~100mA for 900 seconds before stopping. No peaks were observed for the nickel and titanium electrode feeder. In between 1800 secs to 1890 secs, the charged passed during discharge was 90C at the first cycle and 180C at 1800 secs for the charge. The cell voltage at the first cycle during charge was 2.2V at 0.22Watt. Hr. (0.00022Kilowatt. Hr.). For the second cycle of charge
The titanium electrode feeder incorporated to the cell cathode-side as the third investigated current collector has a specific electrocatalyst coating on it for the evolution and reduction of Bromine (Br\(_2\)). [The material has an attractive catalytic coating on it.]

and discharged, the charged voltage was also 2.2V and the charged passed was 181C in between 1890 secs to 3700 secs. Furthermore, the charge passed during discharge was 90C in between 3700 secs to 3790 secs. The charged passed during the third cycle of charge and discharge was 170.5C in between 3790 secs to 5495 secs instead of 180C. However, considering the discharged, 90C was the charged passed in between (5495 secs) and (5585 secs) at approximately 90 secs.

**Carbon vs nickel.**—

Cycle-1

1. Charge Efficiency (CE)

\[
\frac{\text{Charged Recovered (Discharge)}}{\text{Charged Input (Charge)}} \times 100\% = \frac{90}{180} \times 100\% = 47.5\%
\]

2. Energy Efficiency (EE)

\[
\frac{\text{Energy Recovered (Discharge)}}{\text{Energy Input (Charge)}} \times 100\% = \frac{190 \times 0.5}{400 \times 1.7} \times 100\% = 13.97\%
\]

Cycle-2

3. Charge Efficiency (CE)

\[
\frac{\text{Charged Recovered (Discharge)}}{\text{Charged Input (Charge)}} \times 100\% = \frac{200}{310} \times 100\% = 64.5\%
\]
Figure 16. (a) Carbon and Nickel at a current rate of 0.1A and −0.1A for (1), for (4000 secs and 1900 secs), and (2), for (3100 secs and 2000 secs), and (3) for (3000 secs and 1900 secs). (b) 3-Cycles of Charged and Discharge at a Current Rate of 0.1A and −0.1A for (1800 secs and 900 secs), (1810 secs and 900 secs), and (1705 secs and 900 secs) via using the Nickel Vs Titanium with 3M of KBr (535.51g), 1M of KCl (111.89g) as the cathode-side electrolyte and 3M of ZnBr2 (675g), 1M of ZnCl2 (205g), and 1M of KCl (111.826g) as the anode electrolyte solution (c) Cyclic voltammetry at 25mV/s taken after investigating the Nickel and Titanium Electrode.

Figure 17. Bar Chart of Charge-(Blue) and Energy-(Orange) Efficiency at a Current Rate of 0.1A and −0.1A for (1), for (4000 secs and 1900 secs), and (2), for (3100 secs and 2000 secs), and (3) for (3000 secs and 1900 secs). with 3M of KBr (535.51g), 1M of KCl (111.89g) as the cathode-side electrolyte and 3M of ZnBr2 (675g), 1M of ZnCl2 (205g), and 1M of KCl (111.826g) as the anode electrolyte solution.

4. Energy Efficiency (EE)
\[
\frac{\text{Energy Recovered (Discharge)}}{\text{Energy Input (Charge)}} \times 100\%
\]

Charge Efficiency (CE)
\[
\frac{\text{Charged Recovered (Discharge)}}{\text{Charged Input (Charge)}} \times 100\%
\]

Cycle-3
\[
\frac{200 \times 0.5}{310 \times 1.7} \times 100\% = 18.9\%
\]

6. Energy Efficiency (EE)
\[
\frac{\text{Energy Recovered (Discharge)}}{\text{Energy Input (Charge)}} \times 100\%
\]

\[
\frac{190}{300} \times 100\% = 63.3\%
\]
Charge Recovered * Average Voltage During Discharge
Charge Input * Average Voltage During Charge *100%

190+0.5
300+1.7 *100% = 18.6%

Titanium Vs nickel.—
Cycle-1
7. Charge Efficiency (CE)
Charged Recovered (Discharge)
Charged Input (Charge) *100%

= 90
180 *100% = 50%

8. Energy Efficiency (EE)
Energy Recovered (Discharge)
Energy Input (Charge) *100%

Charge Recovered * Average Voltage During Discharge
Charge Input * Average Voltage During Charge *100%

90+1.005
180+2.06 *100% = 24.39%

Cycle-2
9. Charge Efficiency (CE)
Charged Recovered (Discharge)
Charged Input (Charge) *100%

= 90
181 *100% = 49.72%

10. Energy Efficiency (EE)
Energy Recovered (Discharge)
Energy Input (Charge) *100%

Charge Recovered * Average Voltage During Discharge
Charge Input * Average Voltage During Charge *100%

90+1.005
181+2.06 *100% = 24.25%

Cycle-3
11. Charge Efficiency (CE)
Charged Recovered (Discharge)
Charged Input (Charge) *100%

= 90
170.5 *100% = 52.78%

12. Energy Efficiency (EE)
Energy Recovered (Discharge)
Energy Input (Charge) *100%

Charge Recovered * Average Voltage During Discharge
Charge Input * Average Voltage During Charge *100%

90+1.005
170.5+2.06 *100% = 25.75%

Discussion on 2nd and 3rd feeder electrodes.—Carbon vs nickel.—
The three chronopotentiometry cycles that demonstrated good results can be recommended as a good zinc-bromine battery cell due to their efficiencies. This is as depicted in Figure 17 from bars (1) to (3) on the bar chart. The cell efficiency from the first experiment was 47.5%. The cell also stored and discharge more current during the 1st cycle excluding the 2nd and 3rd cycle of charge and discharge. The second experiment demonstrated an efficiency of 64.4%. The cell efficiency was 63.3% for the 3rd cycle. The second charge and discharge had the best performances, followed by the third experiment and lastly the 1st chronopotentiometry experiment, as shown in Figure 16a.

Titanium vs nickel.—From Figure 18, each cycle (1, 2 and 3) has shown that the cell fully discharged up to (0 volt) during the 3-cycles. Cycle-1 and cycle-2 both have a charge and efficiency of 50% and 52.78, respectively, in comparison with chronopotentiometry-3 that has a charge efficiency of 49.72%. Cycle-1 and cycle-2 charge efficiencies were similar except that cycle-1 was slightly higher than that of cycle-2 by 15%. Cycle-3 had an energy efficiency that was a bit higher that cycle-1 and cycle-2 by 0.86% and 1%.

However, just the 1st and 2nd cycle was presented. The battery cell did not lose any energy but gained more by 2% at the end of the third cycle after charging it at a Current Rate of 0.1A and −0.1A secs of different cycles. (cycle-1) for (1800 secs and 900 secs), (cycle-2) for (1810 secs and 900 secs) and (cycle-3) for (1705 secs and 900 secs). Therefore, the three cycles of charge and discharge had good efficiencies and can be recommended as good zinc-bromine batteries cells. The efficiency of battery cell during the third cycles has a good redox reaction with good electrons flow compare to the other cycles. On the presented bar chart, the charge and energy efficiency of the 3rd cycles by using the carbon and nickel electrode feeder were not included since the cell was interrupted due to leakage. Therefore, just the 1st and 2nd cycle was presented. However, the titanium vs nickel electrode cycles for the 1st, 2nd and 3rd cycles were completed and presented. See the bar chart in Figure 16c.

Conclusions.—Different approaches are currently in use to address problems facing redox flow batteries; particularly on dendrites formation within zinc bromine batteries systems. The experimented fluidised bed electrode in this research has been shown to successfully prevent the problem of dendrites formation, produce sufficiently high mass transport of zinc during charging and discharging and supported the chemical reactions. The fluidized bed electrode was capable of fast electron exchange in the charge and discharge cycle because of the
high surface area. The designed system was capable of fast deposition and dissolution of the metal at low over potential forming part of the electrolyte. The use of small particles has allowed for electron transfer to take place and provide a locus for electrodeposition of the zinc. The numerically modelled and experimentally fluidized bed electrode was highly electronically conductive. It also minimises ohmic losses (high efficiency cell) during charging and discharging; except for the high internal resistance constantly encountered within the cell. This was due to the cell size and enclosed materials; such as the reactors, gaskets, Nafion membrane etc., which inhibited the production of higher charges and energy efficiencies. The high internal resistance observed during most of the electrochemical measurements had contributed to the discrepancies among all the charge and energy efficiencies. However, an improved and modified zinc bromine battery cell electrolyte with a methanesulfonic acid that has a high resistance have also been previously reported. This later significantly demonstrated a reduced internal resistance in between 4.9 ohms to 2.0 ohms but an improved energy efficiency in between 64% to 75%; which was similar to the achieved energy efficiency from the battery cell of this research and almost of similar current (mA). Out of all the explored electrochemical measurement on the investigated feeder electrodes materials, the best result was selected. The carbon-cathode and nickel-anode feeder electrode materials had the best performances. Next to these were the nickel-anode and titanium-cathode. The carbon-anode versus carbon-cathode had the least performance. The titanium versus nickel feeder electrode could have performed better than the carbon versus nickel feeder electrode, if these electrode materials were further charged at higher current rates. Nevertheless, the titanium versus nickel feeder electrodes were the last investigated materials that encountered series of electrolyte sequestering agent problems before reverting it back to normal. These notable complications contributed toward the control measure taken by not running the cell further. The analytical procedure proposed in this research investigated these investigated feeder electrodes performances. This procedure was successful and enabled the recognition of the energy efficiency in terms of three (3) metrics: good, better and best efficiencies. This was possible through the different sets of feeder electrodes materials introduced, as summarized below:

1. Carbon-cathode and carbon-anode at a current rate of 0.2A and −0.1A demonstrated a charge and energy efficiency of (43.3% and 15.63%).
2. Carbon-cathode and nickel-anode at a current rate of 0.1A and −0.1A demonstrated a charge efficiency, CE of (51.3%, 53.3%) and energy efficiency, EE of (12.77% and 13.29%). These results were for 2-cycles of charge and discharge before the cell was interrupted.
3. Furthermore, at a current rate of 0.1A and 0.1A, the carbon and nickel feeder electrode at 3-cycles of charge and discharge further demonstrated charge efficiency, CE of (47.5%, 64.5% and 63.3%) and energy efficiency, EE of (13.97%, 18.9% and 18.6%).
4. At a current rate of 0.4A and −0.4A, the carbon and nickel feeder electrode at 3-cycles of charge and discharge established these charge efficiencies, CE of (28.2%, 35.1% and 32.4%) and energy efficiencies, EE (9.54%, 11.8% and 11.27%)
5. Titanium and nickel at 3-cycles of charge and discharge at a current rate of 0.1A and −0.1A established a charge efficiency, CE of (24.39%, 24.25% and 25.75%)

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