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A Mechanically Rechargeable Zinc-Air Battery for Off-Grid and Remote Power Applications

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Abstract

Non-availability of grid-electricity in remote and rural areas presents a challenge for recharging secondary batteries. Mechanically rechargeable zinc-air batteries should mitigate this problem. This work reports a compact, mechanically rechargeable zinc-air battery built around the framework of an electroformed planar nickel mesh current collector. The battery performance was evaluated in longevity and polarization studies. Design and production of the planar, compact battery chassis was done using CAD and 3D printing. A zinc plate and 4-molar KOH were used for the anode and electrolyte respectively. The cathode is an air-breathing gas diffusion electrode that is pressed into the openings of the nickel mesh current collector. The battery electrodes each have a surface area of 400 mm^2 while the OCV was 1.32 V. From the polarization studies, at a voltage of 1.0 V a load of 710 Ω (or higher) can be imposed on the cell with the voltage remaining stable. The longevity test also shows that whilst powering a mini-DC motor for 6 hours, the polarisation potential depreciated only minimally.

Keyword: Fuel Cells, Metal-air Battery, Electrochemical Power, 3D Printing

1. Introduction

Nigeria's electric power conundrum has persisted for generations. This is particularly perplexing given the huge energy resource endowments of the country which has been adjudged to be more than adequate to fuel much of sub-Saharan Africa's energy demands for several decades (Iwayemi, 2008). The need for stationary power and distributed generation to fast-track electric energy delivery at this stage in the country's development is now more pertinent given the burgeoning population and the urgent quest for economic development. Electrochemical power is gaining popularity in the world today due to its cleanliness, inherent high efficiencies and low environmental impact. Since the energy is produced via an electrochemical process, the process is clean, quiet and two to three times more efficient than fuel burning (Rao *et al*., 2009). Electrochemical power is the key enabler of stationary power and distributed generation; hence its pivotal role cannot be overemphasised. This role has been fulfilled for a long time by the ubiquitous rechargeable lithium-ion battery.

Zinc air battery belong to the subset of primary metal-anode batteries. The unique feature of this battery class is their use of solid metal anodes. Metal–air batteries are attractive because of the inherent high energy storage capacity of metals and the virtually limitless supply of low-cost terrestrial oxygen

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(Fenton et. al. 2022). However, their categorization as "primary cells" implies they are not electrolytically rechargeable.

The idea of mechanically recharging metal-air batteries has been explored over the last 60 years. Witherspoon (1969) described a 1 kW prototype, while Cooper et al (1995) and Koretz et al (1996) both described refuellable zinc-air units for vehicular propulsion. These promising early examples notwithstanding, much of battery research and development work in the intervening years has been skewed in favor of rechargeable lithium-ion batteries.

However, the last decade has witnessed growing concerns regarding the sustainability and questionable environmental credentials of lithium-ion battery technology (Piątek et al, 2021). They are notoriously difficult to recycle and contaminate landfills. Post-lithium-based battery systems are now increasingly being considered (Deckenbach and Schnieder 2023). This has renewed interest in mechanically rechargeable zinc-air battery systems. New and innovative mechanically rechargeable zinc-air battery designs have recently been developed for vehicular propulsion (Bhagirathi 2022), navigational buoys (Caramia and Bozzini, 2014), and portable electronics (Nazir et al. 2024)

Mechanical rechargeability usually entails the physical removal of depleted metal anode and cathode. Whilst mechanical recharging is theoretically possible for all primary batteries, the practical challenges of replacing electrode materials provide very little motivation for mechanical recharging. In the case of metal-air batteries however, this case is notably different. Here, mechanical recharging involves the replacement of only one of the electrode materials, the anode. The cathode is an air-breathing gas-diffusion electrode (GDE) which continuously engages in oxygen reduction reactions (ORR) using freely available atmospheric oxygen. Thus, the impetus for mechanical recharging is significantly increased in the zinc-air battery since it involves replacement of only one electrode.

The task of developing a viable, consumer-facing mechanically rechargeable zinc-air battery is essentially a design problem. The role of cell design on the viability of zinc-air batteries, for non-technical end users, cannot be overemphasized (Mainar et. al. 2024). This task has been approached from different design perspectives. These include zinc flow batteries (Borchers et. al., 2021), flexible Zn-Air batteries (Fang et al., 2021), and hydraulically rechargeable zinc – air battery (Mahlendorf et al., 2021).

In this work, a compact, mechanically rechargeable zinc-air battery design was developed. The design was based on an electroformed planner mesh nickel current collector, with the mesh openings also serving as the gas diffusion layer. It is believed that the small form factor of this design would promote scalability of the design in battery stack arrays.

2. Materials and Methods

2.1 Materials

Activated Charcoal, 5% carbon-supported-platinum catalyst, aqueous dispersion of 60 wt.% PTFE, and ammonium bicarbonate (all from Sigma Aldrich, Germany). Electroformed nickel mesh, 4 M KOH electrolyte, 3D Printer (Da Vinci XYZ Pro), PLA and ABS 3D printing filaments (Hatchbox®, California USA), zinc plate.

2.2 Electroformed planar nickel mesh

A planar nickel mesh was produced by electroforming using graphite permanent anode, a copper-coated PLA mandrel cathode and saturated nickel sulphate electrolyte. The electroforming mandrel, bearing the mesh design in high relief, was produced by 3D printing. Copper conducting paint was

applied into the troughs of the relief pattern of the mandrel, and a common conducting pathway was created from them to a single connection point.

2.3 Design and production of battery components

The design of the battery frame was done using AutoCAD® and the various parts were produced on the 3D printer using ABS plastic filament.

2.4 Zinc anode

The zinc (anode) was produced by sectioning the thick zinc plate into a 20 × 20 × 4 mm square cross-section block and encasing it in a 3D printed ABS pouch.

2.5 Production of Gas Diffusion Electrode

The gas diffusion electrode has a 3-ply structure comprising of a gas diffusion layer (GDL) and a reactive layer, sandwiched around the nickel mesh current collector. The GDL was made to be microporous and hydrophobic. It is produced by mixing activated charcoal with aqueous PTFE using compressed air bubbles. Hydrophobicity is introduced by the PTFE using about 50 ml of aqueous PTFE dispersion diluted in de-ionised water to 200 ml. It was mixed for about 30 minutes with activated charcoal in the 60:40 ratio optimised by Yamamura and Furuya (2008). The resulting solution in the beaker was filtered, dried in an oven at 120 °C for 8 hours and knife-milled into powder. Microporosity was created by knife-milling the dried PTFE-activated charcoal paste with ammonium bicarbonate (ratio 50:50 wt. %). The GDE was compressed around the mesh at the 60 kgF/cm^2 (Gharibi and Mirzaie, 2003) and sintered at 350 °C. During sintering, the sublimation of ammonium bicarbonate occurs, leaving behind a micropores network. The GDL was trimmed to about 400 µm (Yamamura and Furuya, 2008) to facilitate optimal diffusion of air.

2.6 Characterisation of gas diffusion layer

The GDL was characterised using scanning electron microscopy, before and after sintering to observe the distribution and morphology of the pore former, the consequent pore network and other microstructural features.

2.7 Assembly of battery

The complete battery was assembled from the separately produced parts and were joined together using room temperature vulcanizing silicon rubber. A 4 M KOH electrolyte was injected into the electrolyte chamber to complete the battery setup.

2.8 Polarisation and longevity studies

The open circuit voltage of the cell was determined. Also, different levels of loading, from 110 to 1310 ohms, were imposed in the cell and the polarization potential measured. This was used to generate a polarisation curve descriptive of the battery's response to various loading conditions.

3. Result and Discussion

3.1 Electroformed planar nickel mesh

The planar nickel with a mesh opening of 2 mm was produced after 120 hours of electroforming. The mesh produced is presented in figure 1. It was in-laid into the cathode chamber as shown in figure 2.
In this work, a planar mesh approach was used instead of the woven mesh for the current collector. Woven mesh tends to suffer from electrolyte flooding. The problem of flooding occurs when portions

of the current collector dips below the baseline and become completely submerged inside the electrolyte. Such submerged portions are removed from participation in electrode reactions since they cannot form triple-phase boundary (TPB) regions due to the inability of ambient oxygen to reach them. This reduces the effective surface area of the gas diffusion electrode and its current density. The planar electrode ensures the positioning of mesh interface surfaces at the baseline in contact with the electrolyte. Hence, more areas of the current collector will participate in electrode reactions, increasing the effective area of the cell and consequently its output current density.

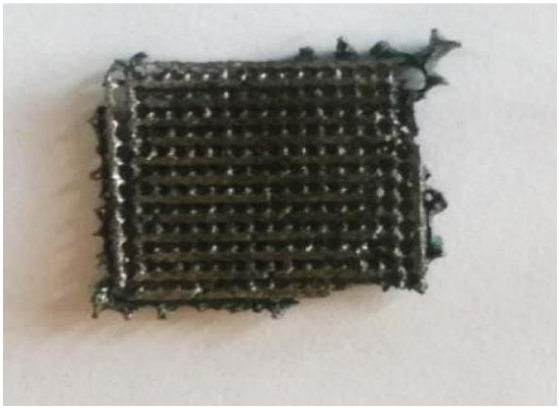

Figure 1: Electroformed nickel mesh current collector

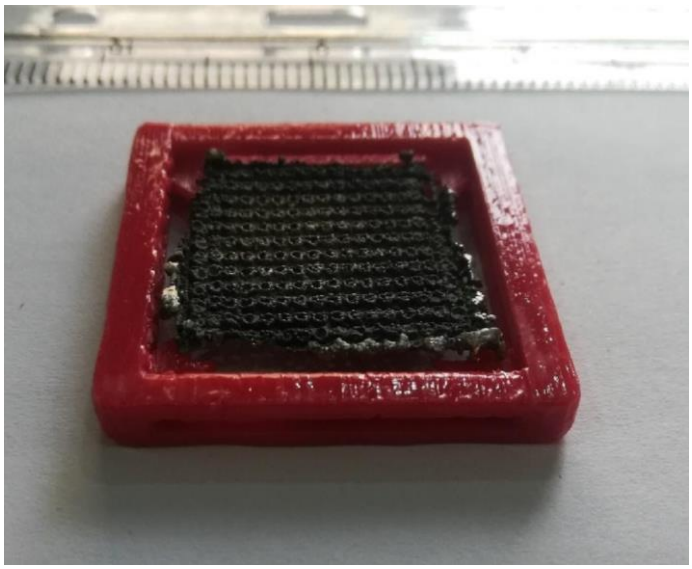

Figure 2: Partial assembly of the cell showing the mesh in position in the cathode chamber

3.2 Production of battery components

The battery component parts produced by 3D printing were assembled and the assembly is presented in Figure 3. The fabricated mechanically rechargeable zinc-air batteries are presented in Figure 4. The use of 3D printing allows for a rapid prototyping of the parts and considerable design flexibility. To reduce the risk of electrolyte leakage, the 3D printed parts were subjected to acetone smoothening the layering patterns that is characteristic of 3D printed parts and through which seeping out of electrolyte can occur.

3.3 Production of gas diffusion electrode

The gas diffusion electrode is a mesh-supported electrode design. This means that the mesh provided the backbone for the other electrode components. Part of the GDL is pressed into the mesh openings, anchoring it in place. The remainder of the GDL, the air-facing portion extends above the mesh by about 400 μm. This portion is crucial; it is microporous and hydrophobic. The pores allow for the

diffusion of air through the air-facing side. The hydrophobicity, imparted by the admixture of PTFE, prevents the leakage of aqueous electrolyte through the micropores. Figure 5 shows the SEM micrograph of the GDL containing adsorbed PTFE particles and ammonium bicarbonate prior to sintering. The positions of some of the PTFE particles are marked by arrow B, while some of the ammonium bicarbonate particles are marked by arrow A.

The SEM micrograph in figure 6 shows the GDL after sintering to 350°C. The presence of cavities at position previously occupied by the ammonium bicarbonate is marked by arrow A. These pores are responsible for permeation of the air molecules to the TPB. Arrow marked B indicate particles of PTFE at the lips of one of the pores. The hydrophobicity of the PTFE particle repels water, preventing electrolyte leakage and flooding of TPB. Ammonium bicarbonate decomposes at about 60°C (Resnik *et al*., 2004), into ammonia, carbon dioxide, and water vapour leaving behind pores in places it previously occupied. Thus, it can be used as a pore former, introducing microporosity into the compacted powder after sintering. This step is important because it permits the diffusion of air (oxidant) into the electrode, turning it into an air-cathode.

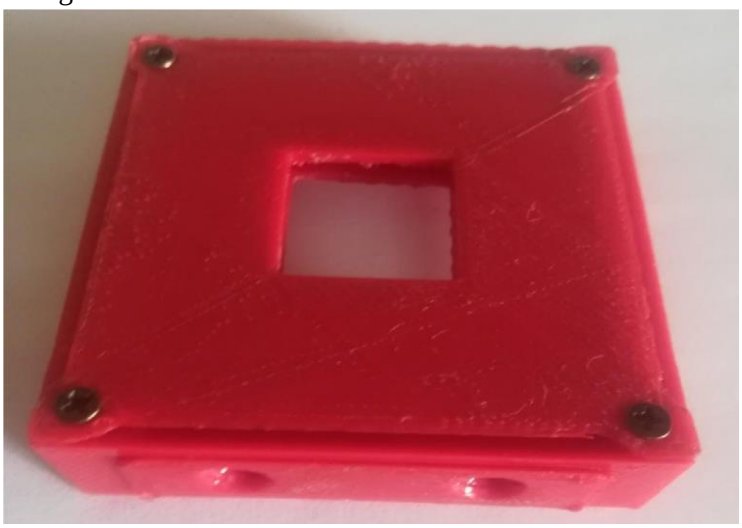

Figure 3: Assembly of 3D printed battery parts

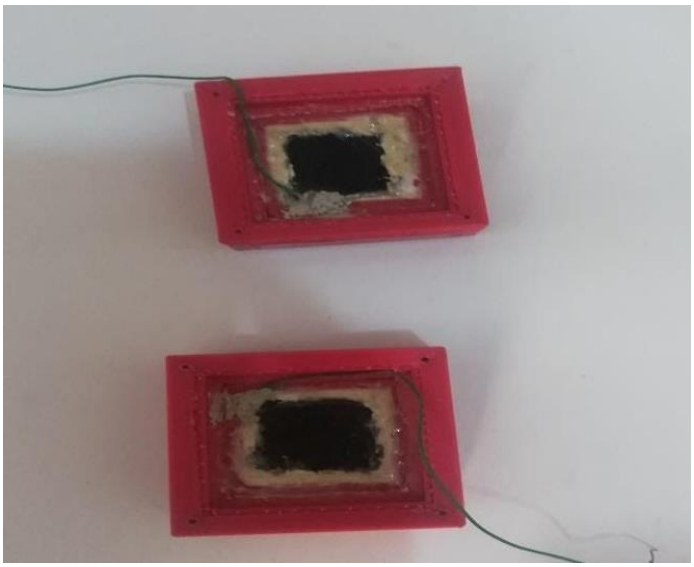

Figure 4: Fabricated Zinc-air mechanically rechargeable batteries

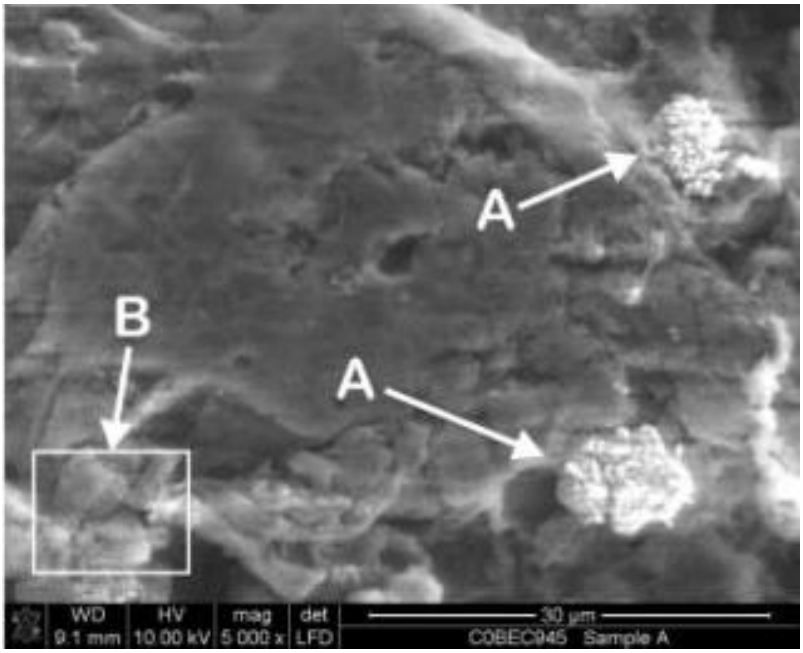

Figure 5: SEM micrograph of un-sintered GDL at magnification of 5000×

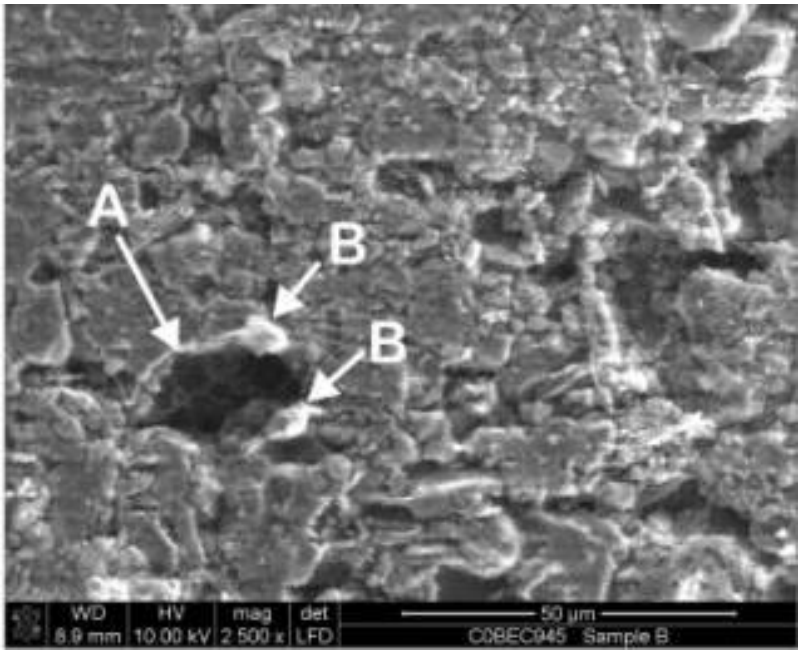

Figure 6: SEM micrograph of GDL showing the pores at 2500×

3.4 Polarization studies

Different levels of load, from 110 to 1310 ohms were imposed on the battery, and the polarization potential measured. This was used to generate a current – potential curve shown in figure 7. The open circuit voltage (OCV) of the zinc-air was found to be 1.32V.

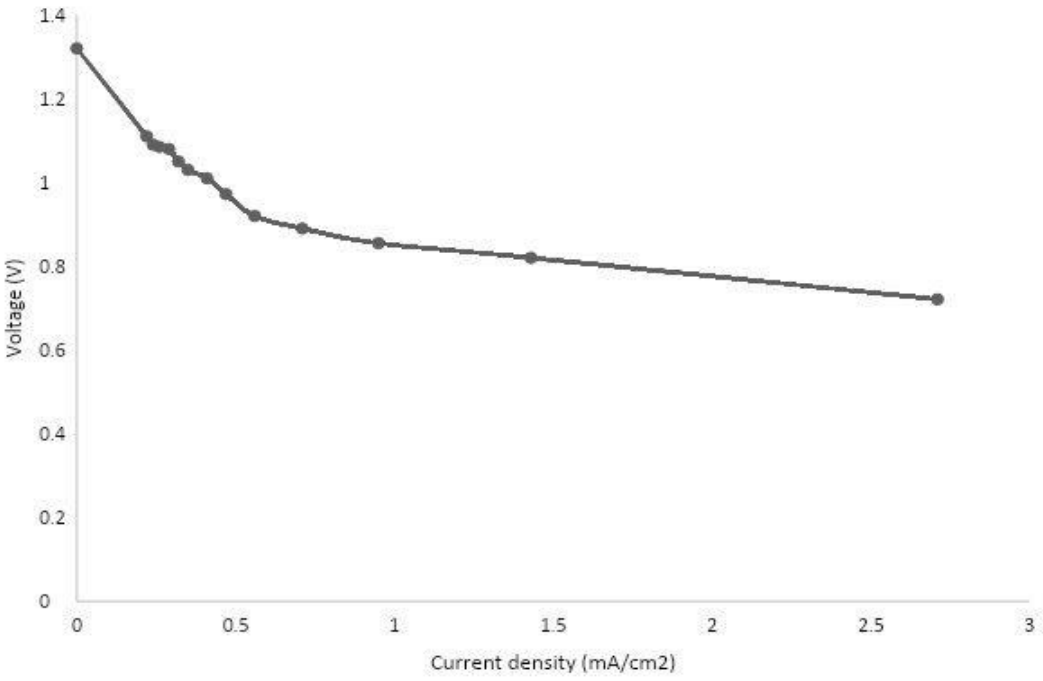

Figure 7: Polarisation curve for cell reaction

The zinc-air battery has a surface area of 400 mm^2. The theoretical value of OCV for a zinc-air battery with 4 M KOH electrolyte is 1.40 V, however the value from the polarization test is 1.32 V. This reduced value is due to the internal resistance of the cell and activation polarisation. From the polarization test carried out, it was deduced that 1V will require a load of 710 Ω or higher. Hence, the lower the resistance, the higher the power generated and the higher the resistance, the lower the power generated.

Figure 8 shows the polarisation curve of the battery when powering a mini-DC motor (rated 1 V) over a period of 6 hours. After initially peaking within the first two hours, the polarisation potential virtually stabilized for the remaining test period of 4 hours. This shows the electrode reactions are stable, and concentration polarisation did not set in.

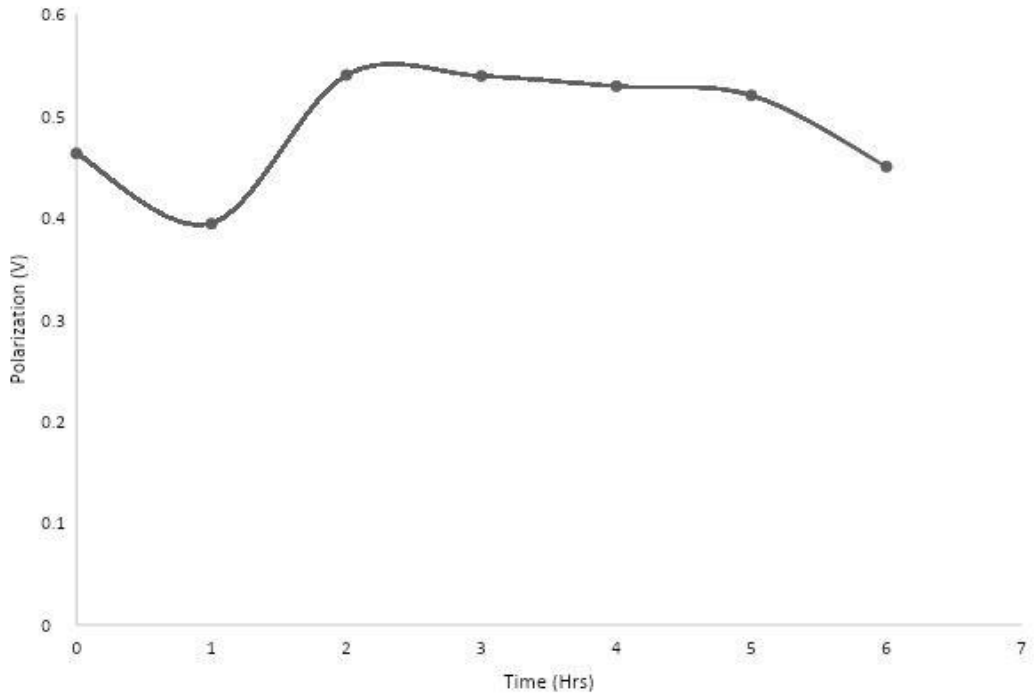

Figure 8: Polarisation Vs. time graph with battery powering a mini-DC motor

4. Conclusion

This work invites a discussion on the need for a paradigm shift in the thinking about electrochemical power and its integration into the mainstream energy supply mix. The prospect of large capacity, swappable anode batteries may help to eliminate the anxiety of power loss from battery drain out as is the case with the popular secondary cells. Furthermore, given the acute absence of charging infrastructure in remote and off-grid areas, a mechanically rechargeable battery may be more appropriate. Such scenarios transcend the typical rural settings and may involve such specialized activities as government-run immunization programs, military operations and telecommunications base-stations that are not easy to serve and resupply with electrical power.

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