IZABW 2023, September 18-19, Stadthaus Ulm

3RD INTERNATIONAL ZINC-AIR AND OTHER ZINC BATTERIES WORKSHOP

BOOK OF ABSTRACTS

ZSW

DLR Deutsches Zentrum
für Luft- und Raumfahrt

3rd International Zinc-air and other Zinc batteries workshop

September 18-19, 2023
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Preface

Primary Zn-air batteries have already been publicly available for a long time as power source mainly for hearing aids and pagers, achieving practical specific energies in the range of 200-500 Wh/kg.In principle, the Zn-air battery chemistry is also suited for rechargeable secondary battery systems by virtue of the relatively low negative potential of zinc, even as an aqueous system. Aqueous Zn-air systems were proposed and built as a promising system long before the dominance of the Li battery systems. However, long-standing bottlenecks hamper their development and commercialization. The main problems were low performance, caused by the inefficient oxygen reaction kinetics and the poor cycling stability, which is attributed to the anode.

Despite the great successes of Li-ion batteries, discussions about to battery systems based on easily available resources with high user safety and low environmental toxicity are on the rise. In this context Zn-air batteries are again in the focus of interest. Over the last decade, significant progress has been made regarding secondary Zn-air batteries by optimizing the anode structure, using additives or alternative electrolytes, as well as developing more effective oxygen catalysts.

The international exchange of experiences has proven to be a good approach for accelerating the developments. Therefore, the German Federal Ministry of Education (BMBF) initiated the 1st International Zn-Air Battery Workshop (1st IZABW) in April 2016 as part of the international R&D project Zinc/air batteries with innovative materials for storing regenerative energies and grid stabilization (LUZI). Since the initial workshop went well, the BMBF suggested repeating this workshop every 2 years as part of an IZABW series. Hence, an advisory board consisting of industrial and academic experts was formed to determine content and location of the respective next workshop. The 2nd IZABW was then organized by SINTEF Energy Research within the framework of the European project ZAS (Zinc-air secondary batteries based on innovative nanotechnology for efficient energy storage) in April 2018 in Trondheim (Norway).

Subsequently, it has been decided to have the third workshop (3rd IZABW) scheduled for 2020 in Germany again. Unfortunately, this date had to be postponed to 2023 due to the Covid-19 crisis.

The 3rd meeting will once again have its focus on the Zn-Air system but will also be extended to other systems such as Zn-ions and other Zn-based systems for further interconnection of the community. A wide variety of presentations and posters from academia and economy will depict the rich and the broad scope of research activities, as well as recent technical developments and the roadmaps towards battery products, hence providing an overview on the current state of the art.

We wish all participants of the 3rd IZABW a successful and productive conference with intensive and beneficiary discussions.

Finally, the organizers want to thank the German Federal Ministry of Education and the Belgian company Everzinc for their financial support, which greatly helped for the organization of the 3rd IZABW.

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within the frame of the project Zinc-Air Battery for Stationary Electricity Storage (Grant number: 03XP0505A)

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Third International Zinc-air and other Zinc Batteries Workshop (3rd IZABW)

18th/19th of September 2023, Ulm Germany, Stadthaus Ulm

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09h00-09h25		#T11 Dr. Nian Liu *Georgia Institute of Technology* USA
09h25-09h50	***Workshop opening*** ***Welcome address***	#T12 Hirotaka Mizuhata *Sharp Corporation* Japan
09h50-10h15	#T01 Dr. Pascal Verbiest *Everzinc* Belgium	#T13 Dr. Alberto Varzi *Helmholtz Institute Ulm* Germany
10h15-11h00	**Coffee Pause / Poster session**	**Coffee Pause / Poster session**
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Conference Schedule

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#T12 Hirotaka Mizuhata, Sharp Corporation (Japan)
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#T14 Milind Dukle, Godrej & Boyce Mfg. Co. Ltd. (India)
Exploring Opportunities for Rechargeable Zinc-Manganese Dioxide Battery Energy Storage Systems

#T17 Dr. Vincent Caldera, EasyIZinc (France)
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#T21 Dr. Ehsan Faegh, Imprint Energy Inc. (USA)
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#T22 Dr. Christoph Müller, Grillo-Werke AG (Germany)
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#T03 Atsunori Ikezawa, Tokyo Institute of Technology (Japan)
Design of Bifunctional Air Electrodes Based on the Reaction Fields in Porous Gas Diffusion Electrodes

#T04 Dr. Roman Kapaev, Bar-Ilan University (Israel)
Carbon-based cathodes for non-alkaline Zn-air batteries: structure-performance relations and anodic stability

#T05 Dr. Krzysztof Dzięcioł, Forschungszentrum Jülich (Germany)
Operando investigation of zinc plating and stripping in KOH, NaCl and ZnSO$_4$ using laboratory XCT

#T06 Prof. Hajime Arai, Tokyo Institute of Technology (Japan)
Zinc electrode rechargeability observed by optical measurement and X-ray diffraction

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Free standing oxygen electrodes for metal-air batteries made up from electrospun carbon-nanofibres

#T18 Prof. Tatsumi Ishihara, Kyushu University (Japan)
Zn-air Rechargeable Battery using Ni$_3$N/ NiCo$_2$O$_4$ Spinel Oxide Air Electrode

#T19 Joachim Hering, TU Braunschweig (Germany)
Multifunctional Additive Blend to Mitigate Dendrite formation in Zinc-Ion-Batteries

#T20 Estíbaliz García, CIC energieGUNE (Spain)
Gel Biopolymer Electrolyte Based on Naturally Occurring Agarose for Quasi-Solid-State Zinc-air Batteries

Please note only the presenting author and his/her respective affiliation are indicated in the present tentative schedule. Full co-authors list and their respective affiliations are provided in the respective abstracts.

The role of zinc-based batteries in the energy transition

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The energy storage market is predicted to grow at a pace of 200 to 500 GWh/year by 2030. With high pressure on lithium battery materials to supply the exponential growth of the EV industry, the need for sustainable alternative chemistries is becoming more clear every day that passes.

Zinc is affordable, sustainable and safe, and is expected to meet the key performance requirements to succeed in this market. This presentation will provide a large picture of the role that zinc batteries will play in the energy transition and a global review of the recent developments in rechargeable battery technologies.

Talk 02

Advanced manufacturing and characterization of printed 3D porous Gas Diffusion Electrodes (GDEs) for Zn-Air Batteries

K. Yezerska[1*], M. Kohl[1], M. Reisch[1], D. Fenske[1], J. Schwenzel[1]

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Currently, different battery technologies suitable for stationary energy storage exist on the market. The most mature technology is Pb-acid, followed by Li-ion batteries (LIBs) which is preferentially integrated for transport. While Pb-acid batteries have low CapEx, they suffer from a short lifetime and low round trip efficiency at high C-rates. LIBs, on the other hand, generally present a better performance than Pb-acid in terms of specific energy and cyclability, but they face significant challenges in costs, environmental impact, safety, and use of CRMs (a challenge to Europe's security of supply). Secondary (rechargeable) Zn-Air batteries (r-ZAB) are among the most promising non-LIB alternatives, with several advantages, with regard to use of aqueous non-hazardous electrolyte systems, inherent safety, low cost as well as its high theoretical volumetric and gravimetric energy density of 6,100 Wh L^{-1} and 1,100 Wh kg^{-1} and finally high abundancy and recyclability.
As a typical battery type the ZAB consists of an anode and a cathode. The crucial reactions which take place at cathode are the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). The cathode is also called gas diffusion electrode (GDE), which consists of a gas diffusion layer (GDL) and a catalyst layer (CL) (Fig. 1a) [1, 2]. The GDE serves multiple functions within the ZAB, including improving ORR, preventing cathode flooding, inhibiting electrolyte evaporation and reduces the production of carbonate and byproducts [1, 3].
This work aims at the development of 3-dimensional bifunctional GDE with using non-precious critical raw material (CRM)-free catalysts and 3D structured corrosion-resistant carbon materials. This will be fabricated using printing technology, specifically screen printing. The bifunctional GDE will be developed by utilizing a screen printing that employs a chess pattern (Fig.1b). Furthermore, the printed GDE will be electrochemically compared to a commercially available GDE as a benchmark.

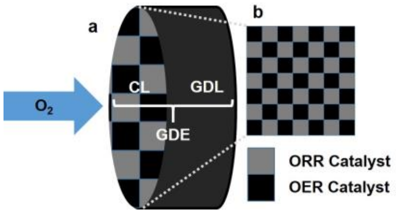

Figure 1: a) Schematic presentation of 3D-GDE structure prepared by screen printing b) chess pattern printing screen.

***Keywords**:* Zn-Air battery, cathode, GDE, printing technology.

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Design of Bifunctional Air Electrodes Based on the Reaction Fields in Porous Gas Diffusion Electrodes

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Zinc-air secondary batteries using alkaline electrolyte solutions are promising candidates for next-generation large-scale energy storage systems. However, large overpotential of bifunctional air electrodes hindered their wide applications. Recently, research on electrocatalysts for oxygen reduction reaction (ORR) and oxygen reduction reaction (OER) has actively been conducted to improve the overpotential, and many highly active catalysts have been developed. On the other hand, forming reaction sites is also critical because the reaction sites for ORR and OER are basically different[1]. In this work, we investigated the reaction sites in porous gas diffusion electrodes (GDE) by comparing oxygen diffusion resistances among different conditions and constructed a GDE with a bilayer catalyst layer based on the difference in the reaction sites for ORR and OER[2].

Oxygen diffusion resistances were estimated from the difference in the steady-state potential between pure oxygen and air atmosphere[3]. Oxygen transport properties of electrolyte solutions affect oxygen diffusion resistances for ORR, indicating that dissolved oxygen is the main reaction species in the ORR process. In contrast, oxygen transport properties of electrolyte solutions have almost no impact on oxygen diffusion resistances for OER, which shows that oxygen is mainly transported as bubbles in the OER process. In addition, oxygen diffusion resistance is almost independent of the catalyst layer thicknesses for both ORR and OER. These results suggest that the reaction fields for ORR and OER are concentrated on electrolyte and air sides of the GDE, respectively.

Based on the above finding, we constructed a GDE with a bilayer catalyst layer (CL), where ORR and OER catalysts were placed on electrolyte and air sides, respectively. The GDE with the bilayer CL showed smaller ORR and OER overpotentials than the GDEs with the monolayer CL and reverse bilayer CL, where ORR and OER catalysts are reversely arranged. Furthermore, the cyclability of the GDE with the bilayer CL is also superior to that of the monolayer CL and reverse bilayer CL. These results verify the assignment of the reaction fields and show the effectiveness of the rational catalyst arrangement on the activity and the durability of the bifunctional air electrodes.

This work was partially supported by JRP-LEAD with DFG Grant Number PJSJRP20221602 and JSPS KAKENHI Grant Number JP23K13819.

***Keywords**:* bifunctional air electrode, porous gas diffusion electrode, reaction field.

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2. Ikezawa, A.; Seki., K; Arai, H.; *Electrochim. Acta* **2021**, *394*, 139128.
3. Kaisheva, A.; Iliev, I.; Gamburzev, S.; *J. Power Sources* **1984**, *13*, 181-195.

Talk 04

Carbon-based cathodes for non-alkaline Zn-air batteries: structure-performance relations and anodic stability

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Rechargeable zinc-air batteries (ZABs) are highly promising for energy storage due to their attractive theoretical energy density, affordability and safety. The primary focus of research is on ZABs that employ alkaline electrolytes, such as 6M KOH. However, alkaline ZABs suffer from serious drawbacks. This includes uneven electrodeposition of zinc, passivation or continuous corrosion of the anode, irreversible absorption of CO_2 from ambient air and corrosion of carbon cathode scaffolds. These issues result in severely limited cycle life and low practical energy density of the devices. A promising way to overcome these limitations is to use non-alkaline electrolytes. This can significantly improve stability of zinc anodes and suppress vertical growth of Zn. It also enables usage of ambient air without CO_2 uptake that leads to cell failure in alkaline ZABs. However, non-alkaline ZABs remain poorly developed, especially at the cathode side that suffers from slow oxygen reduction/evolution kinetics. Designing cathodes with high catalytic activity in near-neutral media is crucial for ZABs.

Here we present a systematic study of carbon-based cathodes in ZABs utilizing aqueous solutions of $Zn(OAc)_2$, $ZnSO_4$ and $Zn(OTf)_2$ as electrolytes. We distinguish structure-performance relationships for materials with varying particle size, graphitization degree, specific surface area, wettability, and surface chemistry. Furthermore, the stability of the cathode scaffolds is evaluated using online electrochemical mass spectrometry and complementary techniques. The findings of this work offer a guideline for designing cathode scaffolds for non-alkaline zinc-air batteries.

Operando investigation of zinc plating and stripping in KOH, NaCl and $ZnSO_4$ using laboratory XCT

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The evolution of active material morphology is of interest when assessing the performance of the metal-air systems [1]. Investigating system dynamics requires an *operando* testing protocol with sufficient temporal and spatial resolution. Typically, synchrotron radiation is employed, as seen in the work of Yufit et al.[2], where synchrotron X-ray computed tomography (SXCT) was combined with FIB/SEM to visualize the dendritic growth of anodic material in zinc-air battery. However, this approach is often economically impractical and unfeasible for longitudinal studies that involve multiple cycling conditions with varying current or electrolyte concentration. Therefore, the statistical power of existing studies might be questioned. In this work [3], we present the *operando* protocol that enables the quantification of active material evolution using strictly laboratory X-ray computed tomography (XCT).

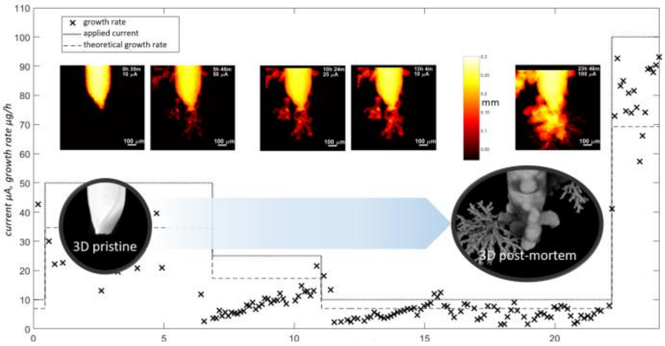

Figure 1: Evolution of morphology of Zn electrode immersed in NaCl

A miniaturized cell was developed and 3D-printed, featuring two ports for zinc electrodes, an electrolyte compartment, and venting holes to mitigate bubbles agglomeration. Imaging was performed, using a state-of-the-art XCT system, specifically the Zeiss Versa 620, achieving a resolution of approximately 0.7 µm at 5 to 7 seconds of exposure. This enabled the capture of up to 1000 radiograms during the 20 to 28-hour-long experiment. Using only radiograms, the material plating/stripping rates were estimated and compared to theoretical values calculated based on Faraday's law. The estimation of material growth from radiograms (2D) was compared to tomographic data (3D) sparsely acquired over time. Finally, the evolution of zinc anode morphology was demonstrated for three different environments: alkaline (KOH), near-neutral (NaCl), and mildly-acidic (ZnSO4).

Keywords*:* XCT, operando, morphology, zinc anode, plating, stripping.

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(2) Yufit, V.; Tariq, F.; Eastwood, D. S.; Biton, M.; Wu, B.; Lee, P. D.; Brandon, N. P. Operando Visualization and Multi-Scale Tomography Studies of Dendrite Formation and Dissolution in Zinc Batteries. *Joule* **2019**, *3* (2), 485–502. https://doi.org/10.1016/j.joule.2018.11.002.
(3) Dzieciol, K.; Durmus, Y. E.; Tempel, H.; Kungl, H.; Bauer, A.; Eichel, R.-A. Laboratory XCT Imaging Protocol Allowing Operando Investigation of Electrode Material Evolution in Various Environments. Rochester, NY February 22, 2023. https://doi.org/10.2139/ssrn.4366144.

Zinc electrode rechargeability observed by optical measurement and X-ray diffraction

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Understanding the charge-discharge mechanism is essential to enhance the performances of zinc electrodes. For this purpose, we have developed an operando measurement system suitable to zinc electrode observation, which includes laboratory X-ray diffraction (XRD) and confocal optics [1]. Thanks to the highly penetrating Mo-K radiation, the structural information of the system can be obtained including the crystallinity growth of Zn/ZnO and diffuse scattering possibly from the electrolyte during the cell operation. The confocal system can adjust the optical focus to the height-changing electrode surface, enabling the spatial distribution of Zn/ZnO, which ultimately affects the shape change of the zinc electrode. With the use of an identical cell for both analysis, the complicated zinc electrode morphology changes as well as the effect of various operating parameters can be well understood.

Several additives that can potentially reduce ZnO solubility were selected among hydrophilic organic materials [2] and the effect on the cyclability of the zinc electrode was evaluated. An effective additive showed a turn-over-number several times larger than that of the system without additives. The additive was shown to enhance homogeneous ZnO precipitation during discharging and promote homogeneous and fine metallic zinc deposition during charging. With the aid of the operando analysis, it was revealed that the additive can assist the uniform reaction process, leading to the restricted shape change of the zinc electrode. As shown in Fig. 1, the diffuse scattering observed during the cell operation suggests the presence of dissolved or low-crystallinity zinc species in the electrolyte. The effect of other additives will be reported in the conference.

Acknowledgment: This work is partially based on results obtained from a project commissioned by NEDO (JPNP21006) and partially supported by JSPS KAKENHI Grant Number 21K14712.

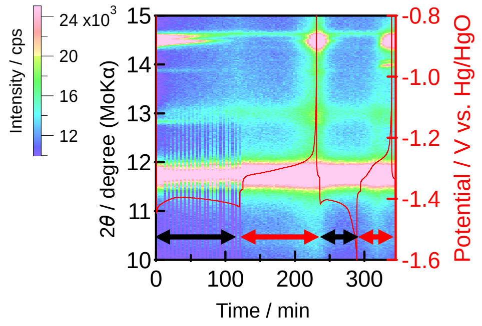

Figure 1: Operando X-ray diffraction of ZnO composite electrode in aqueous KOH solution containing hydrophilic additive. The black and red arrows indicate the charging and discharging periods, respectively. The diffraction signals at around 14.5°, 13.0°, and 11. 7° correspond to ZnO, PbO added as a H_2 evolution inhibitor, and carbon as a conductive agent, respectively.

Keywords: Zinc electrode, operando analysis, X-ray diffraction, Optical measurement.

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2. Kakeya, T.; Nakata, A.; Arai, H.; Ogumi, Z. *J. Power Sources* **2018**, *407*, 180-184.

Talk 07

Multi-technique synchrotron-based study of Zn anodes for Zn-air batteries

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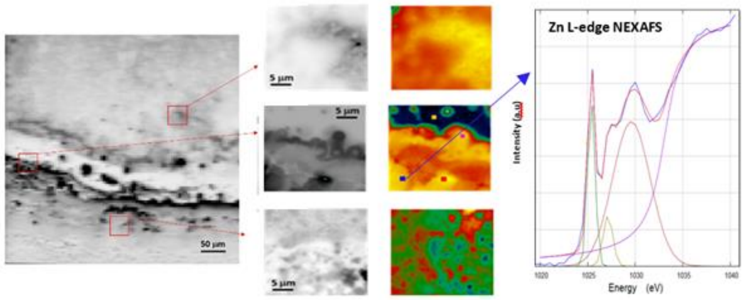
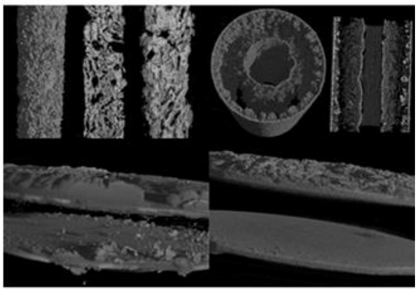
The well-known, but still poorly understood Zn anode shape changes are still a limiting factor of rechargeable Zn-air batteries. In this work, we report a systematic study of electrode and electrolyte engineering, aimed at forming a molecular-level knowledge-based towards the development of stably cycling Zn anodes, revolving around synchrotron-based three-dimensional (3D) imaging[1-3] and chemical-state sensitive spectral imaging[4,5], accompanied by *in situ* vibrational[6] and optical spectroscopy and mathematical modelling[7]. *Post mortem* and *in situ* X-ray computed microtomography-based investigation of Zn electrode cycling for a range of novel chemistries and configurations, at current densities and depths of discharge of practical interest. 3D imaging in intact cells revealed unprecedented morphochemical details of anode shape changes that could be rationally correlated with operating conditions. Moreover, *in situ* and *ex situ* X-ray absorption spectromicroscopy with different electrolytes allowed to pinpoint the synergistic role of morphology and interfacial chemistry in the SEI formation and evolution during discharge/charge cycles. The availability of 3D and chemical-state sensitive information open-up new routes for knowledge-based anode material design and the definition of rational charge/discharge policies.





***Keywords**: X-ray absorption spectroscopy, STXM; hyperspectral mapping, X-ray microtomography.*

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Talk 08

Game-changing breakthroughs in Ni-Zn battery development: RNZB in LOLABAT project for stationary energy storage

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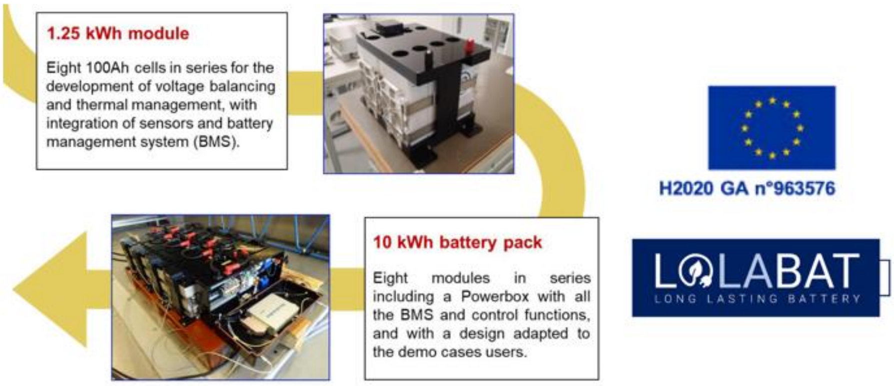
Battery energy storage systems (BESS) are currently seen as important technological enablers for increasing the absorption of RES (renewable energy sources) into the electric grid as a critical step to slow down the climate changes, to overcome the energy crisis and to ensure energy independence between different regions of the world. For the EU with current commitments of reduction of greenhouse gas emissions by 40% until 2030, the complete batteries value chain and life cycle must be considered, from access to raw material, over innovative advanced materials to modelling, production, recycling, second life, life cycle and environmental assessments. SUNERGY's NiZn battery technology with a high actual performance, the pioneering among the already industrialised or near industrialisation Zn technologies, addresses properly the recycling and resources issues, with high potential for improvement. The rechargeable NiZn battery (RNZB) developed at SUNERGY until 2020, is now being promoted and prepared for a future industrialisation via collaboration of 17 partners from 7 European countries through LOLABAT, an H2020 project funded by the European Commission. The RNZB presented and developed during LOLABAT will have energy and power densities both the highest just after Li-ion batteries, cost the lowest just after the Lead-acid battery, cycle life of more than 4000 at 100% DoD, while profiting from abundant and available raw materials, non-toxic elements, high safety, no thermal runaway, limited environmental impact and high recycling potential.

***Keywords**: battery, zinc, nickel, stationary, energy, storage*



1.25 kWh module

Eight 100Ah cells in series for the development of voltage balancing and thermal management, with integration of sensors and battery management system (BMS).

10 kWh battery pack

Eight modules in series including a Powerbox with all the BMS and control functions, and with a design adapted to the demo cases users.

Battery packs being developed in LOLABAT project for different use cases

The Development of Energy Dense Rechargeable Zn/CuO Batteries

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Alkaline Zn batteries are a strong candidate for electrical grid storage applications due to Zn's high capacity (820 mAh/g), established materials supply chain and low cost. To realize the highest energy dense batteries, Zn needs to be coupled with a similarly low cost, abundant and high-capacity cathode. CuO (674 mAh/g) is an intriguing high-capacity cathode when paired with Zn in alkaline electrolyte, a battery that until recently has been relegated to the history books as a primary system. In 2021 Schorr et al. reported a rechargeable Zn/CuO battery that utilized a Bi additive to help facilitate the electrochemical reversibility of the Cu conversion electrode. Bi_2O_3, a species with comparable redox potentials to Cu_2O, promoted reversibility and minimized passivation in the historically non-reversible system. The battery cycled without any observable Cu and Bi mixed oxide phases, cycling between metallic Cu and Bi and $Cu_2O/Cu(OH)_2$ and Bi2O3, respectively. Although the Bi additive did not eliminate capacity fade completely, limiting the cells to a 30% depth of discharge (relative to CuO) enabled 250 cycles at > 124 Wh/L. Seeking to improve performance and minimize the spatial segregation of Cu- and Bi-phases observed upon cycling in the prior system, D. Arnot et al. prepared nanoscale carbon coated (Cu/Bi) particles, where the coating partially minimized dissolution and diffusion of soluble cuprate and bismuthate complexes, where ~ 200 cycles at 300 mAh/g was demonstrated (@ ~ 100 Wh/L). In this case, $CuBi_2O_4$ and CuO phases were formed upon oxidation, indicating carbon coatings can affect the battery cycling mechanism and may have future roles increasing performance. Data collected from a variety of experimental techniques, including cyclic voltammetry, rotating ring-disk electrode voltammetry, electrochemical impedance spectroscopy, electron microscopy, transmission electron microscopy, Raman spectroscopy, operando energy-dispersive X-ray diffraction measurements, battery cycling along with recent DFT modeling will be presented to help elucidate the role of additives, carbon coatings, and ion selective polymers in enabling reversible Cu-based cathodes. The general challenges of achieving a highly reversible energy dense battery based on two conversion electrodes operating in highly alkaline environment will be discussed as will development towards a > 200 Wh/L industrially relevant Zn/CuO battery.

Keywords*:* Zinc, Copper Oxide, gris storage.

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Zinc-Based Rechargeable Batteries Developed in RISIG2/RISING3 Projects in Japan

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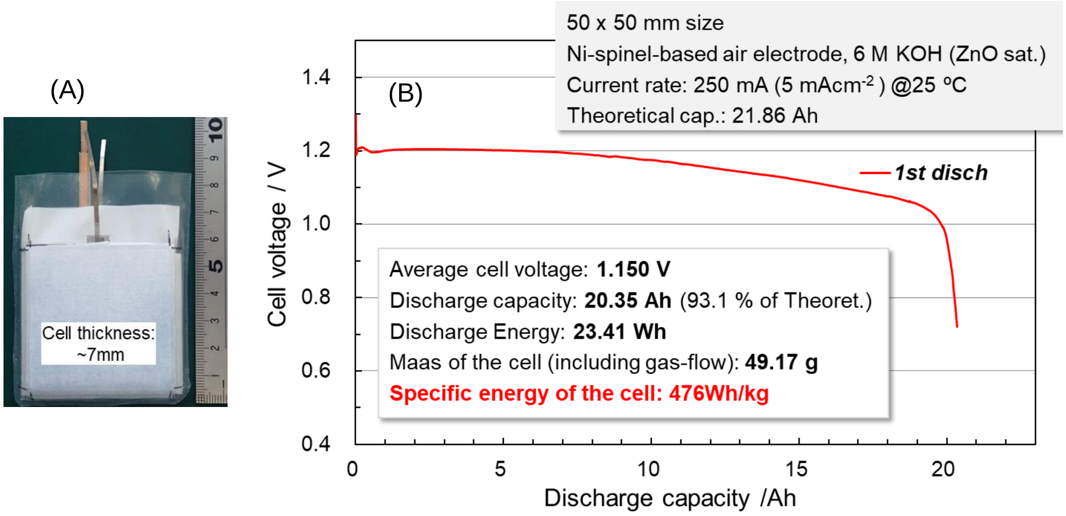
Batteries using zinc (Zn)-based negative electrodes with aqueous electrolytes have a great advantage of constructing inexpensive and safe energy storage systems. Among them, Zn-air batteries (ZAB) that utilize oxygen in the air as an active material for a positive electrode have the highest theoretical energy density of the systems using aqueous electrolytes. Despite the long history of the research and development, there have been no practical system realized on the rechargeable ZAB. The main reasons that hinder their practical use are insufficient energy efficiency and low cycleability of both Zn negative and air positive electrodes. In RISING2 (Research and Development Initiative for Scientific Innovation of New Generation Batteries2) project, systematic collaboration among academia, industry and government in Japan has successfully proved the feasibility of a practical high specific energy battery (ca. 500 Wh/kg : Fig.1) with sufficient cycle life. The details of the elemental technologies and cell engineering established in the project will be presented. The research plan of the succeeding project, RISING3, where the development of sealed battery system using Zn-based negative electrode is the R&D target, will also be mentioned in the presentation.



50 x 50 mm size
Ni-spinel-based air electrode, 6 M KOH (ZnO sat.)
Current rate: 250 mA (5 mAcm^{-2}) @25 °C
Theoretical cap.: 21.86 Ah

Average cell voltage: **1.150 V**
Discharge capacity: **20.35 Ah** (93.1 % of Theoret.)
Discharge Energy: **23.41 Wh**
Maas of the cell (including gas-flow): **49.17 g**
Specific energy of the cell: 476Wh/kg

Fig. 1 Appearance (A) and the first discharge curve (B) of a prototype ZAB developed in RISING2.

***Keywords**:* Rechargeable zinc-air battery, High energy density, Sealed zinc-based rechargeable battery

Acknowledgement
This work is based on results obtained from projects, JPNP16001 and JPNP21006, commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

Deeply rechargeable zinc anodes for high-energy rechargeable aqueous batteries

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Zinc-based aqueous batteries are promising alternative to many mainstream battery technologies today, due to the superior safety and broad availability of raw materials. However, existing zinc anodes suffer from either poor cycle life or low utilization in both neutral and alkaline aqueous electrolytes. Passivation, dissolution, and hydrogen evolution are three main reasons for irreversibility of zinc anodes in alkaline electrolytes, which limits the rechargeability and usable energy density. In this talk, I will present our recent works [1-14] on using nanoscale material design to overcome passivation, dissolution, and hydrogen evolution issues of zinc anode, towards a deeply rechargeable zinc-based battery. I will also introduce the battery-gas chromatography quantitative analysis, as well as in situ microscopy methodologies we have developed, to quantify gas evolution side reaction, as well as visualize the reaction on electrodes during operation.

***Keywords**:* battery, zinc, rechargeable.

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Development of discharging and charging units for a zinc air flow battery

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Toward the realization of a carbon neutral society, it is necessary to develop innovative energy storage technology that can levelize output of renewable energy, which is affected by weather and season, at low cost. Flow batteries are electrochemical devices that uses active materials supplied from external tanks for charging or discharging. Flow batteries can decouple “power (W)” and “capacity (Wh)” in principle, allowing them to store large amounts of electricity by simply increasing the volume of the external tank that stores the active materials.

Due to its abundance on earth and high energy density, a zinc air flow battery using zinc slurry as active material for negative electrodes, is a promising candidate for low cost and large-scale energy storage. In this work, we present our efforts to develop discharging and charging units, which are constituents of the zinc air flow battery system [1].

In the discharging unit, zinc oxidation and oxygen reduction reactions take place at the anode and cathode, respectively. We evaluated the effect of zinc slurry properties and flow rate on the discharge performance by using discharging cell with air cathode comprising MnO_2 and carbon black. In the charging unit, zinc electrodeposition and oxygen evolution reactions take place at the cathode and anode, respectively. We evaluated the effect of electrolyte composition and flow rate to realize stable production of zinc particles by using the charging cell with nickel foam anode.

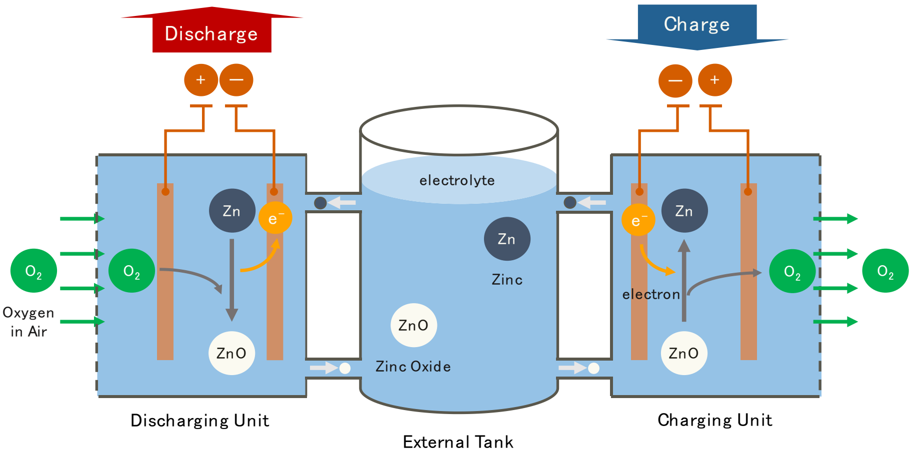

Figure 1: Concept of the zinc flow battery system

***Keywords**: zinc air flow battery, zinc slurry, discharging unit, charging unit*

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Electrolyte and Interphase design for stable Zn anodes

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Aqueous zinc (Zn) batteries have attracted intensive attention from researchers owing to the high theoretical capacity of Zn metal, and its relatively low cost.[1] Accordingly, several Zn-based rechargeable battery systems using alkaline (e.g., KOH solution)[2] as well as close to neutral electrolytes (e.g., $ZnSO_4$ solution) have been proposed.[3] Nevertheless, multiple issues still affect the reversibility of the Zn anode, such as Zn dendrite formation and water/oxygen-related side reactions.[4]

To address the above mentioned issues, substantial efforts have been made following two main strategies: (i) modification of the electrolyte composition and (ii) development of the artificial interphases on the Zn anode.[5] The electrolyte modification is usually aimed at suppressing side reactions with the solvent by reducing the content of free water and optimizing the Zn ion solvation. Herein, highly concentrated aqueous solutions based on low-cost acetate salts will be discussed as promising F-free electrolytes for highly reversible Zn stripping/plating.[6] With regards to the modification of the Zn anode surface, several approaches to form an artificial Solid Electrolyte Interphase (SEI) have been explored in recent years. Here two examples will be discussed, including the design of a thin and uniform ZnF layer obtained by a facile chemical/thermal treatment at the relatively low temperature [7], as well as a Silica/PVDF-HFP-based hybrid interphase applied by a simple solution casting technique [8].

Keywords*:* Zn anode, water-in-salt electrolyte, artificial SEI.

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Talk 14

Exploring Opportunities for Rechargeable Zinc-Manganese Dioxide Battery Energy Storage Systems

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Rechargeable zinc-manganese dioxide ($ZnMnO_2$) batteries can serve as an effective energy storage medium in various stationary energy storage applications, including power backup and solar microgrids. This presentation will explore recent field demonstrations of rechargeable $Zn\text{-}MnO_2$ battery energy storage systems (ESS) to understand the benefits, limitations, and applications of this chemistry in real world settings.

Zinc-manganese dioxide ($Zn\text{-}MnO_2$) alkaline battery chemistry has historically been most effectively utilized in primary battery cells, due to its low-cost, high energy density, and excellent safety. Making the chemistry rechargeable, however, has proved challenging due to the poor rechargeability of MnO_2. This has limited the use of $Zn\text{-}MnO_2$ chemistry in secondary battery applications despite the demand for a rechargeable battery with many of $Zn\text{-}MnO_2$'s characteristics. Recent advancements made by the CUNY Energy Institute and Urban Electric Power (UEP), have illustrated the viability of rechargeable $Zn\text{-}MnO_2$ batteries by demonstrating high cycle life at near-theoretical levels of utilization of the MnO_2 cathode[1] and blocking of Zn crossover to mitigate poisoning.[2] Further developments by UEP have established the manufacturability of these batteries and the technology's capability for scaled commercial deployment.[3] Additional testing programs with the US Navy, Department of Energy, Sandia National Laboratories, and EPRI have helped validate the battery's performance characteristics and has facilitated UEP's initial field deployments of rechargeable $Zn\text{-}MnO_2$ batteries in stationary ESS.

These recent UEP deployments include a 2MWh power backup system for the San Diego Supercomputer Center, a 120kWh solar-tied storage system at a dairy creamery, and a 13kWh solar microgrid system for a residential home in northern Arizona. After one year of field operations, performance data and implementation experiences have clarified the advantages and challenges associated with deploying rechargeable $ZnMnO_2$ systems in these settings. This presentation will review these system deployments, identify opportunities for industry collaboration and application optimization, and explore future commercial prospects for rechargeable $Zn\text{-}MnO_2$ battery ESS.

Figure 1. Solar microgrid (left) and agricultural power backup (right) systems using rechargeable $ZnMnO_2$ batteries.

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Talk 15

Reversible zinc storage for hydrogen production

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Zinc storage electrolysers or zinc-hydrogen storage systems combine the functions of a battery and an electrolyser in one unit. It can be charged during periods of cheap renewable energy and discharged on demand, delivering both electricity and hydrogen gas. During the charging step, as in an electrolyser, oxygen is produced at the gas electrode, but no hydrogen at the counter electrode. Instead, zinc oxide/zincate dissolved in the electrolyte is reduced to metallic zinc and deposited there. The hydrogen production does not require an external supply of energy, but the cell works like a battery, producing electricity and hydrogen simultaneously at low potential. While the primary (only rechargeable) type of this system has been demonstrated previously [1], recharging is now possible thanks to a cycle-stable bifunctional catalyst that switches between HER and OER for each cycle [2,3]. Combined with a fuel cell, the overall reaction is that of a rechargeable zinc-air battery. However, many of the previously unsolved problems of rechargeable zinc-air batteries are solved or do not occur here. One of the most critical issues, the reversible cycling of the zinc electrode, has been solved. Thanks to a special electrical control scheme of the charging and discharging process, between 500 and 800 full cycles have been achieved with a capacity between 4 and 16 mAh/cm^2. The corresponding high cumulative capacity of the zinc anode has not been reported elsewhere.

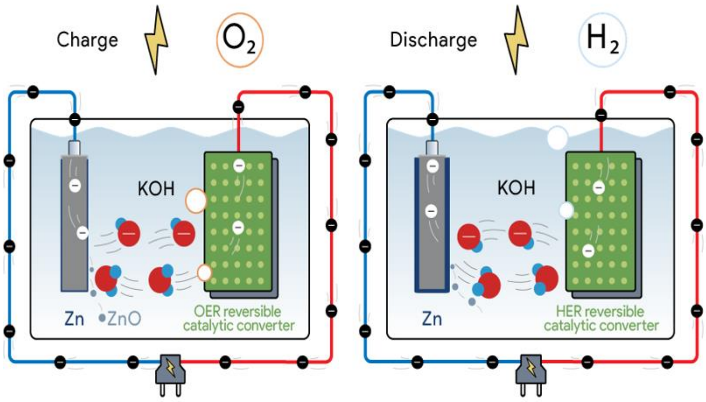

Figure 1: Basic principle of the Zn-H2 storage system

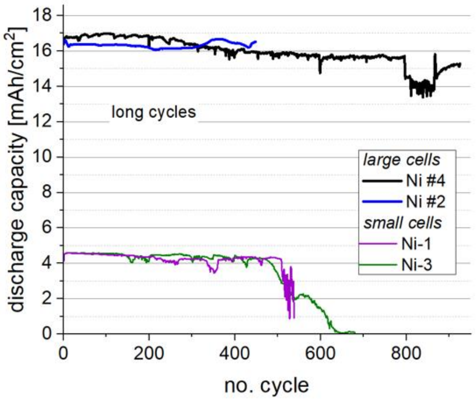

Figure 2: Full cell long term cycling results

***Keywords**: rechargeable zinc electrode, bi-functional HER-OER catalyst, energy storage, KOH.*

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Talk 16

Free standing oxygen electrodes for metal-air batteries made up from electrospun carbon-nanofibres

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Julian Borowec[1,2], Florian Hausen[1,2], Roland Schierholz[1], Emre Durmus[1]
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Performance and stability of the oxygen electrodes are two of the main limiting factors for a commercial application of zinc-air batteries. Current research addresses this issue with developments of new types of catalysts and concepts for the design of the electrode structure. Among these approaches electrodes built from a framework of carbon nanofibres might open the perspective to provide current collector free, free-standing oxygen electrodes with high surface area and catalytic activity for ORR due to nitrogen heteroatoms in the carbon structure. Moreover, transition metal catalysts can be integrated to the fibre structure in a one step process concomitant to the fibre preparation.

The present work summarizes results on structure, morphology and electrochemical performance of oxygen electrodes made up from PAN derived carbon-fibres. The first part of the investigation is concerned with the impact of the carbonization temperature (T_c) during fabrication of additive free carbon fibres on their properties and performance. Along with variation of T_c between 600°C and 1000°C substantial changes in structure and heteroatom content of the carbon fibres were detected. As a consequence, electronic conductivity and catalytic activity are modified, which results in changes of the electrochemical performance with respect to ORR depending of carbonization temperature. In electrochemical experiments in half cells (Flex Cell PP) with 6 M KOH electrolyte, free-standing electrodes from fibres carbonized at 900°C show the best ORR performance.

In the second part of this work the effect of decoration of the carbon fibres with cobalt, integrated in the fibres by adding cobalt(II) acetylacetonate to the electrospinning solution is investigated. Size and distribution of the cobalt particles emerging on the surface of the fibres depend on the carbonization temperature. Compared to the catalyst-additive free fibres, the addition of Co-precursor modifies the graphitization of the fibres and decreases their nitrogen content. An enhancement by a factor of 3 in ORR current density compared to the optimum additive-free fibre electrodes (T_c = 900°C) was obtained in electrodes made up from Co-containing fibres. Further development of this electrode design approach is required by improving the in-plane conductivity of the electrodes.

***Keywords**:* metal air-battery, oxygen reduction reaction, metal-air batteries, carbon fibres.

Recent advances in EasylZinc's innovations for rechargeable batteries

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The research on advanced materials and electrodes as well as their chemistries are essential for Zinc batteries development. At EasylZinc, we focus on the understandings of the fundamental design of these advanced materials and their chemistries in relation to the battery performance.

EasylZinc is a French company located in French Alps that develops active materials and additives for zinc electrodes intented for rechargeable batteries. Strong from an EIC accelerator project named SUPERZINC, we are focusing on the scale-up production of calcium zincate, and its use within zinc negative electrode for wide zinc rechargeable application such as Zinc-Air, Zinc-Nickel and Zinc-MnO_2. This well-known active materials from scientific community have never been industrialized and EasylZinc will be the first company to overcome this huge gap. Starting from its registration under CAS number 55957-39-6, the future of green chemistry is no longer a dream, it is happening now.

This presentation will explain our diversity of activities, from the research to the scale up, this work needs to be done to makes easier the Energy transition. We target our materials to be ready to use by battery manufacturers to allow the better performances possible with a competitive cost. On-site, our materials are tested in prototype cells to evaluate the performances in cycling. Post-test analysis are performed such as, particle size distribution, powder XRD, TGA, cross-section X-Energy Dispersive Signal Scanning Electron Microscopy Mapping (X-EDS-SEM), X-Ray radiography and more.

Optional : Divided in 2 teams, one is working of the scale up to create the pilot production line of the calcium zincate, one is working on prototyping batteries to test materials. 2 speakers can talk about both of activities.

Talk 18

Zn-air Rechargeable Battery using Ni_3N/ $NiCo_2O_4$ Spinel Oxide Air Electrode

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Zn-air battery of which theoretical capacity is 1370Wh/kg is already commercialized as a non-rechargeable one, and mainly applied for the power source of a hearing aid. Because of the cheap cost and safety of Zn, Zn-air rechargeable battery is highly attractive as mobile application, in particular, electric vehicles. At present, increase in cycle stability and energy efficiency which means decreased overpotential of cathode are strongly required. For this purpose, development of highly reversible and stable air electrode is strongly required. In this study, we investigated the modification of $NiCo_2O_4$ spinel oxide with metal nitrate for highly reversible and stable air electrode for rechargeable Zn-air battery.

Figure 1 shows SEM observation results of $NiCo_2O_4$ prepared with hydrothermal synthesis method. Shape of $NiCo_2O_4$ prepared with hydrothermal method is quite unique like stacked needle shape such as flower bouquet. The needle like particle is not single particles but consisted of many small particles with narrow rectangular shape. Considering the XRD, the needle like $NiCo_2O_4$ seems to be oriented along 331 direction which might be 110 direction.

Figure 2 shows charge and discharge property of Zn-air full cell using 5 wt% Ni_3N loaded $NiCo_2O_4$ used for air electrode and 4M KOH electrolyte. In accordance with the ORR/OER cycle measurement, stable discharge and charge curves were observed repeatedly. The observed discharge capacity and the plateau potential were ca.800 mAh/g-Zn and 1.15 V at 50mA/cm^2. Although the discharge potential was decreased with cycle number, discharge capacity of 750 mAh/g$_{\text{-Zn}}$ was sustained over 200 cycles. This means air electrode of $Ni_3N/NiCo_2O_4$ is highly active and stable. Decrease in discharge potential was assigned to the enlarged concentration overpotential of air electrode and this could be assigned to the deposition of $KHCO_3$ which is products of carbon oxidation as discussed above and also flooding of electrolyte in air electrode may be occurred. In any case, highly active and reversible performance of air electrode was achieved on $NiCo_2O_4$ needle which is obtained by hydrothermal synthesis.

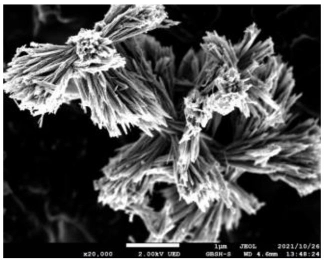

Fig.1 SEM image of $NiCo_2O_4$ prepared with hydrothermal synthesis

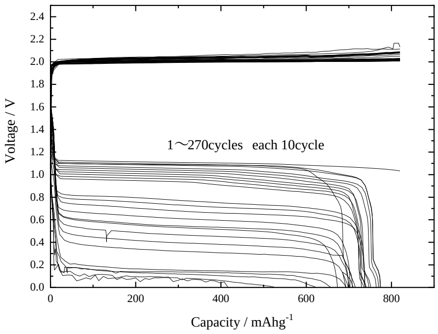

Fig.2 Charge and discharge property of Zn-air full cell using 5 wt% Ni_3N loaded $NiCo_2O_4$ used for air electrode

Keywords: Air electrode, Ni_3N, $NiCo_2O_4$ nanowire

This study was financially supported by RISING2 project from NEDO, Japan (No..16001).

Talk 19

Multifunctional Additive Blend to Mitigate Dendrite formation in Zinc-Ion-Batteries

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Metallic zinc has been used as anode material since the beginning of modern electrochemistry 200 years ago.[1] The high theoretical capacity, low electrode potential and low cost are the main reasons for using zinc as anode material.[1] Currently, zinc-manganese dioxide batteries (ZMBs) with metallic zinc anodes and neutral electrolyte are a promising alternative that could replace lithium-ion batteries in niche applications in the future.[1] However, several issues remain to prevent ZMBs becoming commercially viable . The reversibility of electrochemical reactions at the zinc anode is affected by corrosion, the water splitting reaction and dendrite growth.[1]

For this reason, strategies to inhibit these side reactions are developed in this work. Additives and additive mixtures are tested and their effects on the aforementioned side reactions are quantified and qualified.

In this work, we develop an additive mixture in an 1M $ZnSO_4$ electrolyte that inhibits side reactions even at low concentrations and therefore can be cycled longer and achieve higher Coulomb efficiency in ZMBs. We use the previously published, environmentally friendly and cheap additives Sodium dodecylbenzenesulfonate (SDBS), Ethylenediaminetetraacetic acid (EDTA), and Diethyl ether.[2] SDBS is known to form a layer on the zinc electrodes, leading to more homogeneous growth of zinc in the 002 lattice plane which lays parallel to the anode surface.[2] EDTA changes the solvation sphere of Zn^{2+} in the electrolyte.[2] As a result, less water reaches the anode, leading to fewer side reactions and a more homogeneous distribution of Zn^{2+} along the anode surface.[2] Diethyl ether alters the outer solvation sphere of Zn^{2+} and accelerates Zn^{2+} transport.[2] Thus, adding Diethylether leads to a more homogenous Zn^{2+} distribution and more homogenous plating at the anode.[2] In the end, the optimal combination of these additives to reach higher cycle number is elucidated.

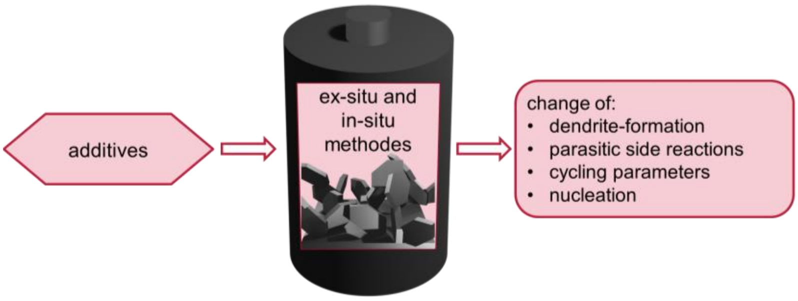

Figure 1: Scheme for the applied Design of Experiments.

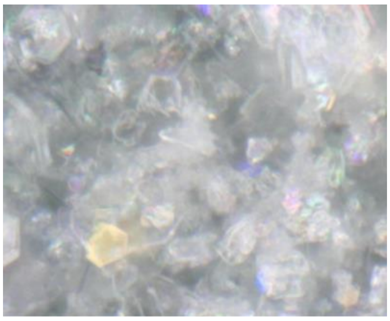

Figure 2**:** Plated Zn out of an 1M $ZnSO_4$ solution at 1 mA/cm^2.

***Keywords**:* Zinc Anodes, Electrolyte additives, Zinc Ion Battery, neutral Electrolyte.

1. Hu, W.; Ju, J. et al., *J. Mater. Chem. A* **2021**, *9*, 25750–25772. DOI: 10.1039/D1TA08184E
2. Wang, D.; Li, Q. et al., *Adv. Energy Mater.* **2022**, *12*, 2102707. DOI: 10.1002/aenm.202102707

Talk 20

Gel Biopolymer Electrolyte Based on Naturally Occurring Agarose for Quasi-Solid-State Zinc-air Batteries

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Portable electronics in the very near future will require batteries with characteristics such as high energy density, flexibility, reliability, rechargeability, and safety at very low cost. In the development of systems with such requirements, rechargeable metal-air batteries arise as a promising alternative due to the use of non-flammable electrolytes and inexhaustible oxygen from air, providing a high theoretical energy density. In particular, zinc-air batteries (ZABs) have attracted a great deal of attention due to the cheap materials involved, environmental friendliness, and safe operation. ZABs are based on abundant elements with excellent stability, high theoretical energy density (1350 Wh kg^{-1}) and theoretical cell voltage of 1.66 V. However, for their practical use, challenges such as low Zn utilization and lifetime for primary ZABs, short cycle life and low power density for secondary ZABs must be overcome. Among them, particularly the electrolyte system plays an essential role in the performance of primary as well as electrochemically rechargeable ZABs, because it is the medium for ionic migration.

In this talk, the development of a gel biopolymer electrolyte based on the naturally occurring agarose polysaccharide will be presented. The biopolymer soaked in a saline solution forms a suitable gel, that not only presents outstanding ionic conductivity, (same magnitude order as 8M KOH solution liquid electrolyte) but also mechanical stability; even after being subjected to a constant discharge until battery failure. The gel does not liquefy, and behaves as an elastic material till up to a certain applied compression load. Experimental data for main physical, chemical, and electrochemical properties, and lab-scale full cells under several testing conditions, are provided to demonstrate merits of the developed gels, and cell design details to be improved.

Talk 21

High power, ultrathin, flexible ZinCore Batteries

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Zinc batteries are attractive alternatives to lithium batteries in a number of applications due to their intrinsic safety, low cost, abundance of raw materials and easier manufacturing process. Specifically, in applications such as wearables and small internet-connected devices zinc chemistries can outperform lithium chemistries in terms of volumetric energy density with respect to thickness, operational temperature, safety, packaging and flexibility. They also are not listed as hazardous goods and don't have limitations on their transport and operation which make them especially attractive for use in smart shipping labels.

Imprint energy has developed ZinCore™: an ultrathin and flexible Zinc battery technology, that can support high power requirements (Figure 1), up to 1500 mW, for cellular applications in a wide range of operating temperatures from -35 °C to 60 °C. ZinCore™ batteries are manufactured using a screen and stencil printing technology in a high throughput sheet and roll-to-roll process. Furthermore, ZinCore™ batteries can be designed in custom sizes and shapes (Figure 2) and configured to provide 1.5V, 3V, 4.5V, 6V etc. running voltage for cellular and Bluetooth devices.

In our presentation, we will discuss power requirements and temperature limits for Internet Of Things (IoT) applications and matching battery performance and size for IoT applications. We will share performance data of ZinCore batteries and Imprint's roadmap for future applications.

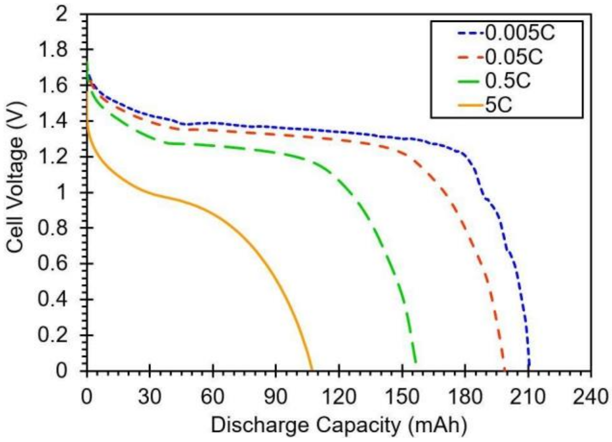

Figure 1: Constant current discharge curves of ZinCore Batteries at different rates.

Figure 2: Imprint Energy's ZinCore batteries in various sizes.

Keywords: Zinc battery, Lithium battery, ZinCore battery, IoT

Zinc Batteries – Yesterday-Today-Tomorrow

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The way to a carbon-free economy often needs creativity and innovation. But sometimes quite old ideas open the way for cheap and sustainable solutions. While everyone is taking about the improvement and availability of Lithium-Ion-Batteries. An element used over 200 years ago in the very first battery, the voltaic pile, by Allessandro Volta can provide many advantages for modern energy storage systems.

Here we present a brief history of zinc-based batteries and where we can find them today. They are in everybody's hand, but hardly being recognized.
Furthermore, we show an outlook on tomorrow's rechargeable zinc-based batteries market. The variety of different cell chemistries requires a variety of different zinc anode materials. We will also take a look at the quality and availability of these materials.

In summary, we present the progress of zinc-based batteries from the very first battery to innovative energy storage systems of today and tomorrow. Also, the versatility of the cell chemistries, possible applications, and materials of these systems is shown. In addition, the required quality and supply chain characteristics of zinc anode materials are reported.

***Keywords**: zinc, battery, energy storage.*

In situ Electron Microscopic Observations of Zinc Metal Depositions in Liquid Electrolytes

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Primary Zn anode batteries have already been commercialized in several forms such as Zn-air and Zn-carbon batteries. However, the development of rechargeable Zn-based batteries faces several problems. These problems include dendrite formation on the Zn electrode during charging–discharging processes, which can cause a short circuit. On the other hand, electrodeposition processes in various kinds of electrolytes still have not been so clear. Preventing dendrite formation requires clarification of the formation behavior and mechanism of Zn dendrites especially at their initial stages. Recently, liquid-phase transmission electron microscopy (LP-TEM) has been employed in *in situ* observations of electrodepositing process of Zn metal. However, LP-TEM observations have a problem with reproducibility of electrochemical reactions due to the thin liquid thickness [1,2]. To achieve reliable control of the electrochemical reactions and *in situ* nanoscale imaging, we designed novel method of electrochemical scanning electron microscope (EC-SEM) as show in Fig. 1 [3]. By using our EC-SEM, reproducibility of electrochemical reactions has been much improved. EC-SEM images of electrodeposited Zn metal onto platinum working electrode are shown in Fig. 2. We will present morphological change of Zn metals depending on electrochemical conditions.

This work is based on results obtained from a project, JPNP21006, subsidized by the New Energy and Industrial Technology Development Organization (NEDO).

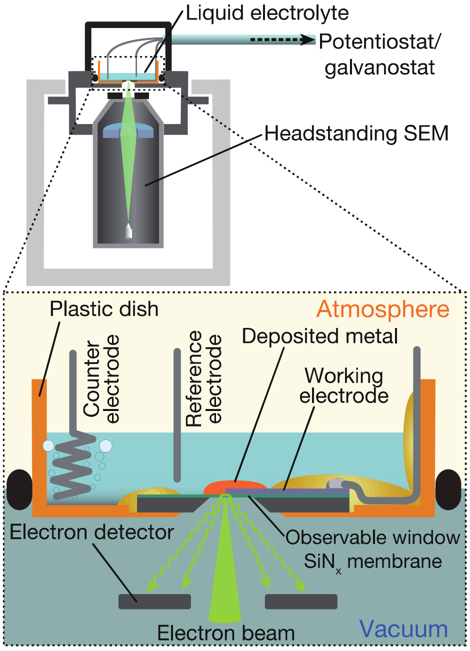

Figure 1: Experimental setup of EC-SEM

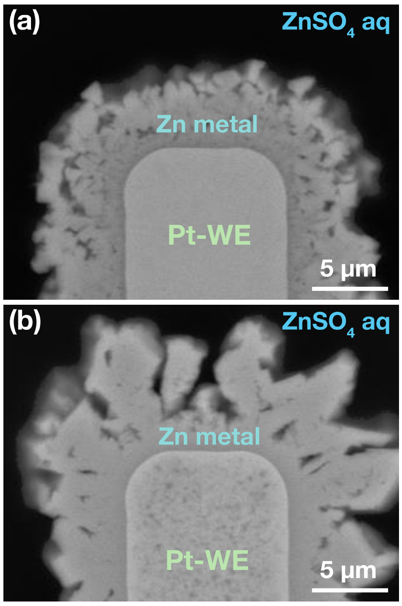

Figure 2: EC-SEM images of Zn metal deposited from 0.5M $ZnSO_4$ solution under constant current conditions of (a) 1 µA for 100 s and (b) 10 µA for 10 s

Keywords: *in situ* observation, Zinc anode batteries, scanning electron microscopy

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2. Sasaki, Y. et al. *J. Electrochem. Soc.* **2021**, *168* (11), 112511. DOI: 10.1149/1945-7111/ac39e0
3. Yoshida, K. et al. *Microscopy* **2022**, 71 (5), 311-314. DOI: 10.1093/jmicro/dfac028

Activated Carbon for Zn-anode Battery

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For the Zn-Carbon rechargeable battery, various kind of activated carbons were investgated as the cathode. The chemical activated Activated Carbon Fibers (ACF) showed much higher discharge capacity than the conventional steam activated carbons. Observation of the microstructure of chemical activated ACF revealed that carbon layered structure was developed and mesopores were abundant. As a result of analysisi of the pore size distribution by NLDFT method, chemical activated ACF had much mesopores ration of 2 nm or more than conventional steam-activated activated carbon. These structural factors are thought to contribute to the high discharge capacity of the chemical activated ACF.

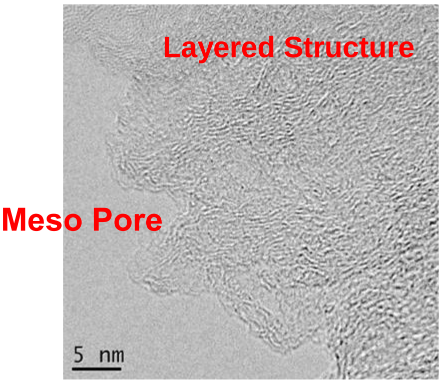

Figure 1: TEM bright filed image of chemical activated ACF

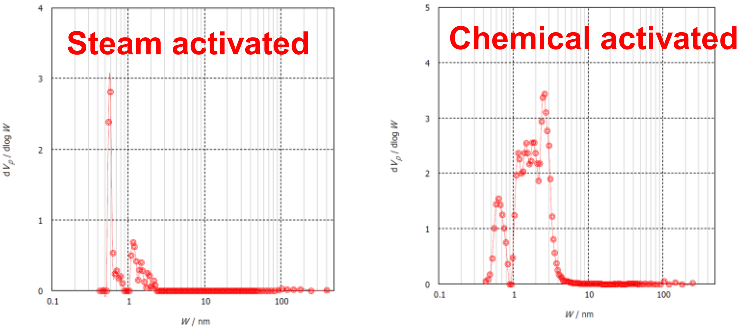

Figure 2: Pore size distribution of stem activated and chemical activated carbon by NLDFT

***Keywords**:* Zn-Carbon battery, ACF, chemical activation, meso pore

Acknowledgement
This work is based on results obtained from a project, JPNP21006, commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

1. Kundu D et al., A high capacity and long‐life aqueous rechargeable zinc battery using a metal oxide intercalation cathode. Nat Energy. **2016,** 1(10):16119.
2. Jaanus Eskusson et al., Zn(ClO4)2 aqueous solution–based Zn thin foil|carbon cloth two‐electrode single‐cell characteristics, *J. Solid State Electrochemistry,* **2021,** 25:2869–2880.

Nickel-Zinc Batteries: Cell Level Modelling and Simulation

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Nickel-zinc (NiZn) batteries are a promising candidate for sustainable energy storage. Such technology is necessary to upgrade the electricity grid to be able to successfully combine the increasing share of renewable energy sources with the growing demand for electric energy. Besides their competitive specific energy and power, NiZn batteries have the advantage to rely on abundant and low-cost resources, environmentally friendly and recyclable materials and non-flammable components[1,2].

While these properties make NiZn cells in principle suitable for this task, the chemical and physical processes taking place are not yet fully understood, which is the basis to create a battery design with high cycle life. Important research topics, which influence cell performance and degradation, are zinc conversion at the anode, proton intercalation at the NiOOH/Ni(OH)2 cathode and gas formation consuming electrolyte, which leads to a dry-out of the cell.

A physics-based 3D+1D model working on volume averages is implemented, which was derived from existing models[3]. Using this thermodynamic framework, a NiZn cell is cycled to examine transport processes and electrochemical reactions. This allows for example to study the distribution of phases (Fig. 1) and chemical species in the battery cell[4].

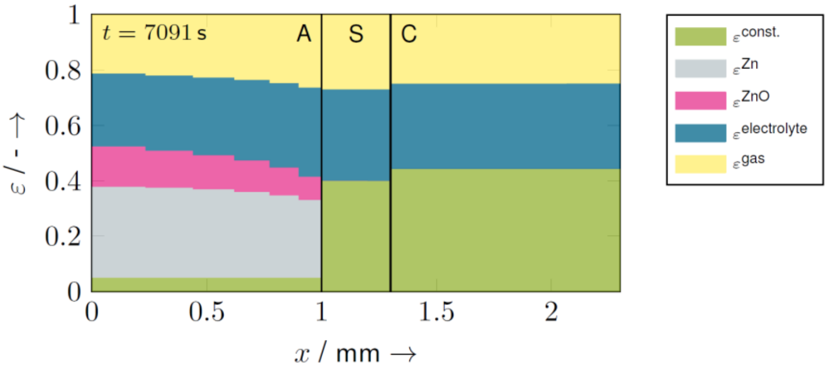

Figure 1: Volume fractions of different phases along the cell's x-direction at time t = 7 091 s.

***Keywords**: nickel-zinc, physical modelling, charge/discharge simulation, zinc shape change*

1. McBreen, J. *Journal of Power Sources* **1994**, *51* (1-2), 37–44. DOI: 10.1016/0378-7753(94)01954-1
2. Reddy, T. B. *Linden's Handbook of Batteries*, 4th ed.; McGraw-Hill: New York, NY, 2011
3. Latz, A.; Zausch, J. *Journal of Power Sources* **2011**, *196* (6), 3296–3302. DOI: 10.1016/j.jpowsour.2010.11.088
4. Schmitt, T.; Arlt, T.; Manke, I.; Latz, A.; Horstmann, B. *Journal of Power Sources* **2019**, *432*, 119–132. DOI: 10.1016/j.jpowsour.2019.126649

Modelling and Simulation of secondary zinc air batteries with anion-exchange-membranes

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The zinc-air battery chemistry is a promising candidate for future energy storage. However, the previously developed cells suffer from significant degradation resulting in poor cycle and shelf life. One of the main degradation mechanisms identified is the carbonation reaction with ambient CO_2 continuously lowering the alkalinity of the electrolyte.

This, amongst other performance decreasing effects such as the presence of high zincate concentrations at the gas diffusion electrode, can be addressed e.g. by incorporating a polymer membrane which is only conductive for single charged anions **[1]**, allowing for the necessary exchange of hydroxide ions OH^- . Both, $Zn(OH)_4^{2-}$ and CO_3^{2-}, are present as multivalent ions in strongly alkaline media, thus their transport is prohibited.

The usage of such membranes is a rather new approach for zinc-air battery cells and needs to be analysed and understood in further detail. One of the common approaches in modern battery research besides experiments is simulation, because it allows access to many variables at any given time and location of the simulated cell under a wide range of environmental and boundary conditions.

Within the ZABSES project, a model for secondary zinc-air batteries with anion conducting polymer membranes is developed. Due to the complexity of the considered system, the model needs to be reduced to incorporate only the main investigated effects. The used volume-averaged continuum model is a combination of reaction rate approximations using approaches such as Butler-Volmer-chemistry and kinetic reaction rates with a model for the electrochemical fluid incorporating e.g. particle and charge conservation.

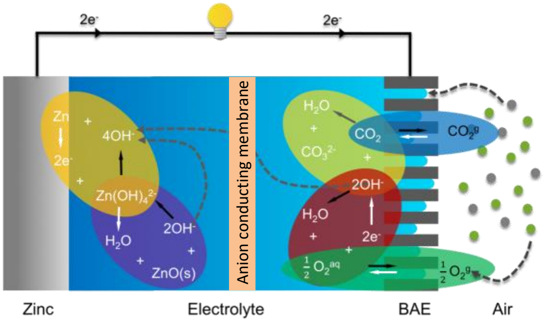

Figure 1 : Schematic representation of cell chemistry **[2]**

This modelling approach has already been used and validated for zinc air batteries by previous research **[2, 3]**. The main goal of the conducted research is the extension of the model to include the polymer membrane as well as further details such as side reactions and degradation mechanisms.

[1] Dembele, K., Chikh, L., Alfonsi, S., & Fichet, O. (2023). Effect of polyelectrolyte architecture on chemical stability in alkaline medium of anion exchange membranes. Polymer Degradation and Stability, 110462.

[2] Stamm, J., Varzi, A., Latz, A., & Horstmann, B. (2017). Modeling nucleation and growth of zinc oxide during discharge of primary zinc-air batteries. Journal of Power Sources, 360, 136-149.

[3] Schmitt, T., Arlt, T., Manke, I., Latz, A., & Horstmann, B. (2019). Zinc electrode shape-change in secondary air batteries: A 2D modeling approach. Journal of Power Sources, 432, 119-132.

Zn-Carbon Rechargeable Battery

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For the Zn-Carbon rechargeable battery, Zn is used for the anode, carbon is used for the cathode, and safe water-based electrolyte is used. Comparing the discharge capacities of various kind of activated carbon as the cathode of the Zn-Carbon rechargeable battery, chemical activated Meso Carbon Microbeads(MCMB) showed higher capacity than the conventional steam activated carbon. It will be discussed that the advantage of chemical activated MCMB has higher electronic conductivity and higher meso pore ratio than the conventional activated carbon.

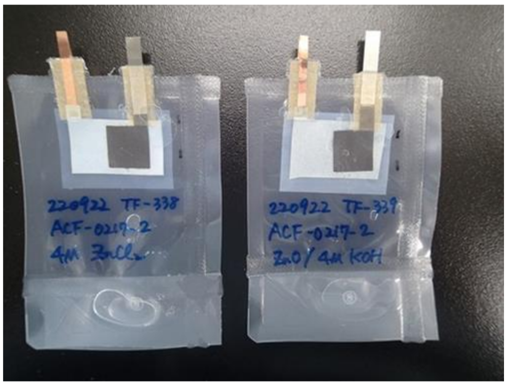

Figure 1: Prototype laminated battery

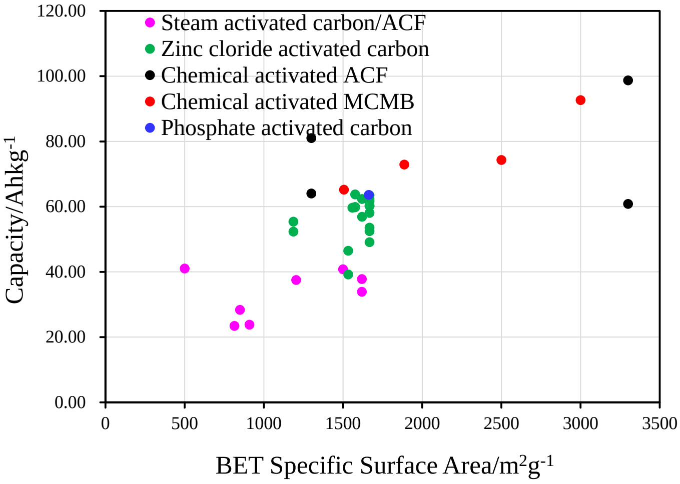

Figure 2: Discharge capacity of Zn-carbon battery using various activated carbons

***Keywords**:* Zn-Carbon battery, activated carbon, chemical activation, meso pore

Acknowledgement
This work is based on results obtained from a project, JPNP21006, commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

1. Tanyanyu Wang et al., Carbonate formation on carbon electrode in rechargeable zinc-air battery revealed by in-situ Raman measurements, *J. Power Sources*, **2022**, *533(15)*, 231237.
2. Jaanus Eskusson et al., Zn(ClO4)2 aqueous solution–based Zn thin foil|carbon cloth two-electrode single-cell characteristics, *J. Solid State Electrochemistry,* **2021,** 25:2869–2880.

Interference of the Reference Electrodes' Leakage on the aging of Copper Hexacyanoferrate for aqueous Zn-ion Batteries

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The repercussions of climate change have shown that global warming is occurring faster than predicted, pushing further the need of a bigger spread of renewable energies, leading thus to the development of acqueous metal-ion batteries [1]. Among the these systems, aqueous Zn-ion batteries have gained considerable interest due to their low-cost, high safety and non-toxicity. As material for the positive electrode, Prussian Blue-analogue Copper Hexacyanoferrate (CuHCF) has attracted great attention thanks to its in- expensiveness and easy synthesis procedure [2]. Generally, a three-electrode setup containing a reference electrode (e.g. Ag/AgCl or SCE) is used to study the active material. Here, we show that the ions leaked from the reference electrode can interfere with the aging and cycle life of the active material, with a reliance on the cation. In particular, an increasing amount of potassium leaked from the reference electrode's solution has shown over time to have a negative effect on the lifespan of CuHCF. Conversely, at lower concentrations it appears to have a slight beneficial effect. A leakage simulation of sodium chloride, instead, shows a weaker influence at higher amount and a modest effect at minor concentrations, indicating an overall smaller influence on the active ma- terial's aging and cycle life. Therefore, using sodium in the reference electrode's solution might lead to more reliable results in case of unexpected leakage, while contamination by potassium could bring to deceitful measurements.

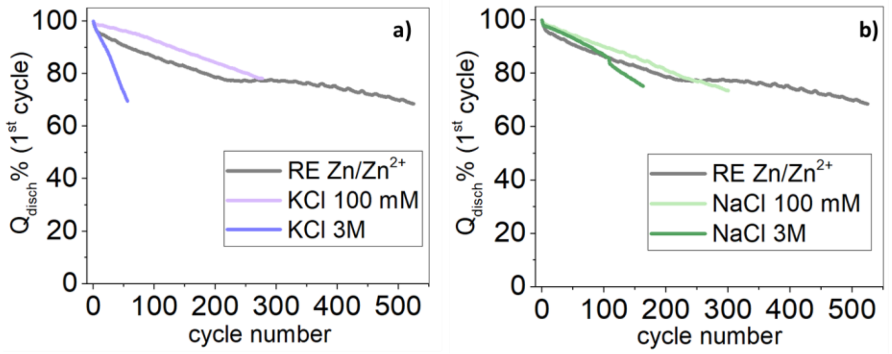

Figure 1: Capacity retention of CuHCF cycled in 100 mM $ZnSO_4$ vs Zn/Zn^{2+} with an increasing simulated leakage of *a)* KCl and *b)* NaCl.

Keywords: aging, aqueous Zn-ion batteries, CuHCF, electrolytes impurities.

[1] J. Tollefson, Nature **2022**, *Climate change is hitting planet faster*.
[2] G. Zampardi, F. La Mantia, Curr Opin Electrochem **2020**, 21, 84–92.

Approaching an anode-free Zinc-Air Battery A future lightweight Technology for Energy Storage

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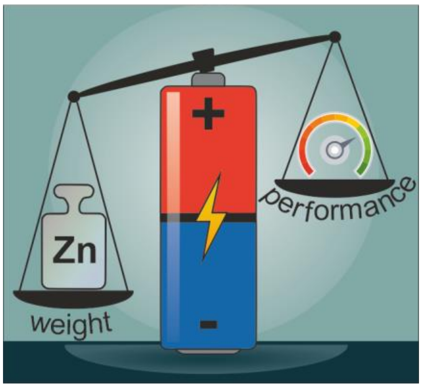
The current developments of rechargeable zinc-air batteries still use significantly oversized zinc anodes, as it is found in zinc-air primary cells already for decades. Unlike the primary cell, which can only make one-time use of the zinc reservoir that was previously installed, our approach towards a rechargeable, secondary zinc-air battery has the distinct advantage of being able to replenish spent active material. This would allow to reduce the zinc reservoir significantly, thus achieving enormous savings in terms of weight and resources. For an anode-free zinc-air battery, the zinc reservoir would be minimal since there is no or only minor zinc deposit on the anode side. Employing this idea would enable a sustainable processing in which the zinc metal in the cell is constantly used in a circular process. The active zinc material is solely generated from the electrolyte volume by plating within the charging process. Anode-free zinc-air batteries thus facilitate electrode balancing, since the charging process can then be used to control which amount of energy is to be stored. Whereas in most known current anode configurations the active zinc species has to be retained as close as possible to the anode, the diffusion of the zinc species in anode-free secondary zinc-air cells into the electrolyte volume can be tolerated and allows for the first time to bypass the typical anode degradation phenomena and thus increase reversibility.[1,2] Thus anode-free concepts have the potential to open up a new avenue in the development of rechargeable zinc-air batteries.



Keywords*:* zinc-air battery, zinc-ion battery, rechargeability.

[1] Deckenbach, D.; Schneider, J.J.; A 3D hierarchically porous nanoscale ZnO anode for high energy rechargeable zinc-air batteries, *Journal of Power Sources* **2021**, 488, 229393

[2] Deckenbach, D.; Schneider, J.J.; A long overlooked pitfall in rechargeable zinc-air batteries: proper electrode balancing, *Adv. Mater. Interfaces* **2023**, 2202494.

Synthesis of porous Fe-NC microcapsules as active catalysts for oxygen reduction reaction in Zn-air batteries

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There has been a strong demand for reversible catalysts for the air electrode of Zn-air batteries because of the sluggish kinetics of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Precious-metal-based catalysts such as Pt/C or IrO_2 have limited cycle stability and high cost. Therefore, developing low-cost, highly stable, and active catalysts is a major task to the practical Zn-air batteries. Zeolitic imidazolate frameworks (ZIFs)-derived nitrogen-doped carbon (NC) catalysts, which possess high surface area and abundant active sites, have been attracting attention as air electrode catalysts due to their high ORR activity[1]. In this study, NC microcapsule particles with both mesoporous and microporous structures are synthesized with spray pyrolysis method, and their air electrode activity is examined.

In the spray pyrolysis method, precursor solvent is transformed into nano-sized droplets by ultrasonic atomizer. The generated droplets are then carried into a tubular furnace set at a specific temperature and calcined. Zinc oxide is produced during calcination, resulting in hollow microcapsule particles that reflect the precursor droplets. To obtain ZIF-8, zinc oxide is mixed with 2-methylimidazole and calcined in Ar to create NC. Additionally, metal-loaded NC is synthesized by adding metal salts to the precursor solution.

The NC catalysts exhibited hollow microcapsule particles that were maintained from the zinc oxide particles synthesized with the spray pyrolysis method as shown in Fig.1. The synthesized nitrogen-doped carbon catalysts were amorphous structure. In metal-loaded NC, metal nanoparticles with a uniform size of about 20 nm are distributed on the NC microcapsule. The catalysts have both microporous and mesoporous structures, which were derived from the structure of ZIF-8, the spray pyrolysis and calcination, respectively. This porous structure led to a high surface area higher than 700 $m^2\ g^{-1}$.

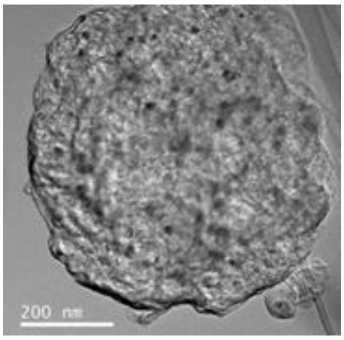

Fig.1 TEM image of Fe-NC

The NC catalysts derived from ZIF-8 showed high activity to ORR, and the activity was significantly increased by loading metal. In particular, Fe loaded NC (Fe-NC) showed similar activity to Pt/C (Fig.2). Fe-NC also exhibited high ORR stability over 300 h as air electrode measurement using a half-cell. A mixed catalyst consisting of Fe-NC and Ni-Fe layered double hydroxide (LDH) exhibited high stability for both ORR and OER over 500 cycles.

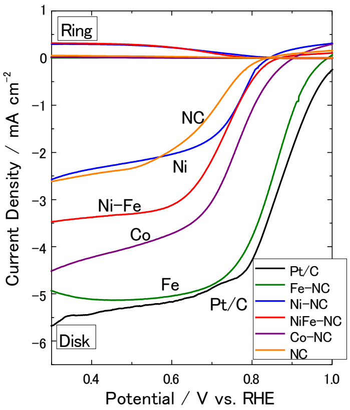

Fig.2 ORR activity of NC catalysts

Keywords*:* N-doped carbon, Fe loading, air electrode

1. Hai-xia Z. et al. *Angew. Chem. Int. Ed.* **2014**, *53*, 14235-14239.
   DOI: 10.1002/anie.201408990

Verbundprojekt ZiMaBat

„Wiederaufladbare Zink-Mangan-Batterie mit pH-neutralem Elektrolyten”

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A successful energy transition depends on innovative and efficient electrochemical energy storage technologies. In view of limited lithium and cobalt deposits and their foreseeable price development, it is not possible to cover the energy storage requirements with Li technologies alone.

The goal of this project is the development of rechargeable aqueous zinc ion batteries based on manganese cathodes (ZMBs) with an energy density of 170 Wh/L and at least 50 charge/discharge cycles in AA format. For this purpose, a high energy prototype (E-ZMB) and a high performance variant (P-ZMB) will be advanced. Detailed pH dependent degradation mechanisms such as Zn dissolution, dendrite formation, Mn dissolution/deposition and corrosion processes of passive components are elucidated in order to determine an optimal pH range. Apart from pooling expertise in the fields of zinc and manganese chemistry, separators and battery construction, a consideration of recycling issues and accompanying LCA studies will complete this project.

Project funded by “Federal Ministery of Education and Research” as part of “BMBF-Förderinitiative Batterie 2020 Transfer“, project no 03XP0481A-H.

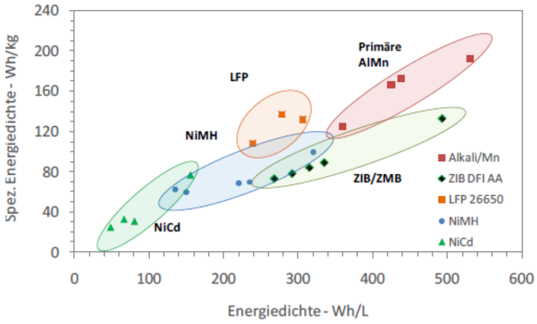

Figure 1: Energy Density of storage systems [1]

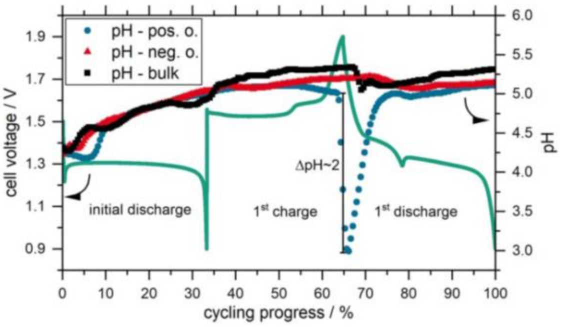

Figure 2: ZMB - pH during cycling [2]

***Keywords**: ZMB, Energy Density, pH range*

1. Reddy, T.B..; Linden, Handbook of Batteries, 4. Edition **2008**, Chapter 28.4.2
2. Bischoff, C.F., Fritz O.S, et al. Journal of the ECS 167, **2020**, 020545

Prussian-Blue Analogue based Zinc-ion batteries for stationary storage applications

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Society faces a steadily growing need of energy, which, in order to make the energy transition happen, cannot be covered by limited fossil fuels. This way, renewable energies and the associated necessary energy storage technologies, e.g. batteries, are of more and more importance for the scientific research. Especially in the field of stationary storage, these storage solutions have to be cost-efficient, harmless for the environment, safe and need to provide high power in order to enable fast charging or discharging depending on the needed energy (peak shaving).

Here, aqueous zinc-ion batteries seem to be an excellent candidate, due to their non-toxic and non-flammable electrolyte, their high specific power, high reversibility and sustainability, due to the overall abundant as well as low cost zinc. Next to the metallic zinc anode, which allows for fast cycling, the zinc-ion battery consists of a respective positive electrode. For the cathode side several material classes can be applied. Particularly, Prussian-blue analogues (PBA), like copper hexacyanoferrate (CuHCF) or manganese hexacyanoferrate (MnHCF), show excellent coulombic efficiencies and have high lifetimes, while their synthesis is easily scalable, which is inevitable for later application in stationary energy storage.

In this contribution we will present our results on scaling up the PBA synthesis of CuHCF and MnHCF to a post lab scale (10g per day) and will show the electrochemical performance of these materials in a demonstrator full cell with an active area of 140 cm^2.

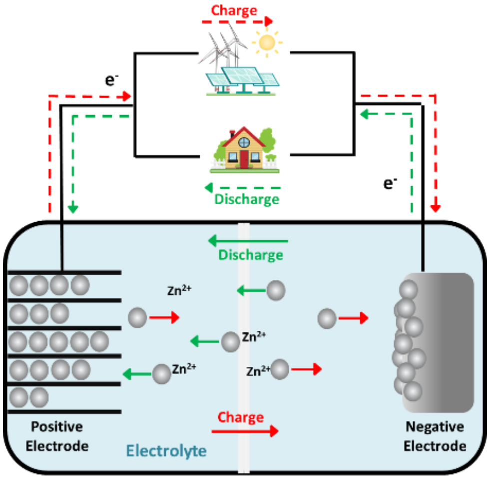

Figure 1: Schematic depiction of an aqueous zinc-ion battery

***Keywords**: Prussian-Blue Analogues, aqueous Zinc-ion battery, up scaled synthesis*

Composite gas-diffusion electrode (CGDE), containing carbon and zeolite, for rechargeable zinc-air batteries

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Metal-air batteries, particularly zinc-air systems that use rechargeable air and metal electrodes, are of great interest due to their increased energy consumption and attractive component characteristics. The development of gas diffusion electrodes (GDEs) is based on gas-permeable and alkali-electrolyte-resistant gas diffusion materials, which form a gas diffusion layer (GDL). The aim of the current investigation is to improve the oxygen diffusion in the GDE. A number of carbon and non-carbon materials with porous, layered, and fibrous structures that possess gas diffusion channels have been investigated.

It was found out that the structure of natural zeolites meets these requirements. By partially replacing the teflonized carbon black in the GDL with zeolite, the necessary hydrophobicity can be attained, while maintaining the high gas permeability of the zeolite material. The catalytic layer was composed of a bimetallic catalyst consisting of silver and γ-MnO_2 in a 1:1 ratio. The morphology of the catalytic layer, as well as the pore size in the GDL, were studied using BET and SEM analyses. From the BET analysis, it was found that the pore size (bellow 10nm) implies mainly the occurrence of Knudsen diffusion. In the preliminary durability tests high mechanical, chemical and electrochemical stability (more than 750 cycles) was observed in the newly developed CGDE.

***Keywords**: composite gas-diffusion electrode, zeolite, zinc air batteries*

Acknowledgements: The authors kindly acknowledge the financial support of project № BG05M2OP001-1.002-0014 „Centre of Competence HITMOBIL - Technologies and systems for generation, storage and consumption of clean energy", funded by Operational Programme "Science and Education For Smart Growth" 2014-2020, co-funded by the EU from European Regional Development Fund.

Single layer gas diffusion electrodes (GDE)

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There are still some challenges to making rechargeable metal/air batteries widely used, one of which is finding a cheap, stable, and efficient gas diffusion electrode (GDE). Typically, the GDE is comprised of an active layer (AL) that can catalyze both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) successively repeating respectively during the charge and discharge of the battery. The second component is the gas diffusion layer (GDL), which allows oxygen to pass through to the active catalytic centers (ACC) and prevents electrolyte leakage.

Automating the production of these electrodes is a complex and expensive process. To address this issue, the concept of a single-layered GDE was created, which eliminates the need for a division between AL and GDL. This lack of separation has a number of advantages, including the ability to blend and place both layers simultaneously, the absence of micro-voltages during the reception and operation of the electrode due to the single layer, and a significant reduction in production costs. The developed electrode is built in a single layer with its components (i. e. teflonized carbon black, hydrophilic zeolite - clinoptiolite and PTFE powder) mixed together with a bi-metallic catalyst. Then, a current collector was inserted, followed by sintering. The bi-metallic catalyst used is composed of a mixture of silver powder and nano-sized Co_3O_4.

By controlling the amounts and ratios between the individual components, we can create a synergetic effect that forms a partially hydrophilic, partially hydrophobic 3-D network of pores and channels, providing access of electrolyte and oxygen to the ACC. This network is also partially but sufficiently electrically conductive thanks to the carbon black.

This single-layer electrode achieves acceptable electrochemical parameters for a GDE. It was investigated by SEM, BET, gas permeability, V-A characteristics, and half-cell cycling.

Keywords*:* single layer gas-diffusion electrode, zeolite, zinc air batteries

Acknowledgements: The authors kindly acknowledge the financial support of project № BG05M2OP001-1.002-0014 „Centre of Competence HITMOBIL - Technologies and systems for generation, storage and consumption of clean energy”, funded by Operational Programme “Science and Education For Smart Growth” 2014-2020, co-funded by the EU from European Regional Development Fund.

Improving Cathode Performance with CVD Deposited Copolymer Thin-Films

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Today's metal-air batteries are mostly primary batteries in which the capacity of the battery usually depends on the capacity of the metal electrode. The development of electrically rechargeable metal-air batteries is largely hindered by critical challenges mostly associated with specific metal electrodes. However, electrochemical stability of Bifunctional Air Electrode (BAE) is also important for overall performance of metal-air batteries as there are major challenges related to the reversibility and lifetime of BAE s in which a gas reactant comes in contact with a liquid reaction medium. Although most research efforts focused on synthesis of bifunctional catalysts and carbon-free catalytic layers, the role of Gas Diffusion Layer (GDL) on BAE performance should not be overlooked. Water intake from atmosphere is one of the problems for alkaline metal-air batteries due to formation of insoluble products. The excess moisture also restricts oxygen diffusion through the electrode reducing electrochemical activity of cathode. Water uptake through the cell also reduces electrolyte concentration leading to decreased ionic conductivity and cycling life.

To overcome these problems, AMAZE project investigates the synthesis of novel bifunctional catalysts and the feasibility of using ultra-thin polymer films fabricated via Chemical Vapor Deposition (CVD) for surface modification of catalyst layer and GDL, and also as stand-alone GDL layers. In this work we report the performance of fluorinated siloxane copolymer thin-film GDLs in gas diffusion electrodes for metal-air batteries. Fabricated polymer thin-films exhibited an average water vapor transmission rate of 7.5 g m^{-2} day^{-1} and enhanced oxygen diffusion with oxygen permeabilities as high as 3.53×10^{-15} mol m m^{-2} s^{-1} Pa^{-1} (10.5 Barrer). Cathodes fabricated using polymer thin-films GDLs also showed higher oxygen reduction current densities than commercial cathodes.

***Keywords**: O2 cathode, gas diffusion layer, polymer thin film*

Material-structure-property relations in bifunctional electrodes for metal oxygen batteries - homogenous material synthesis and advanced operando analysis

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Full utilization of renewable energy is mandatory for our future carbon neutral society. Thereby, a balance needs to be found between renewable energy production and society's energy consumption. Accordingly, more and more batteries are needed as large-scale energy storage systems with high energy efficiency and high reversibility. While lithium-ion batteries (LIBs) have been widely used for portable devices and vehicle applications, the use of LIBs for such large-scale energy storage may not be realistic due to their high cost, less abundant constituent materials and insufficient safety standards. In contrast, metal–oxygen (or metal–air) batteries are promising as low-cost and high-energy-density energy storage systems, and can be constructed with abundant and safe materials such as zinc electrodes and aqueous electrolytes[1]. However, metal-oxygen batteries suffer from the poor performance of the oxygen electrode in terms of activity and durability, and further advances in materials research and fundamental understanding are needed.

The overarching project goal is to create a detailed and general understanding of the material-structure-property relations between the catalyst material applied and the electrochemical processes in the well-designed bifunctional electrodes for the use in metal-oxygen batteries. Of special importance is thereby that knowledge and design suggestions for optimal electrodes will be derived. The expected results will be likewise important for the developers of the single cells for metal-oxygen batteries and battery stacks, since they will access optimal electrode designs that enable reduced production costs. The project work will indirectly contribute to the improvement of systems beyond the metal-oxygen battery, such as fuel cells and electrolyzers, to make them more efficient and durable, since they rely on similar electrode materials, structures and electrode geometries.

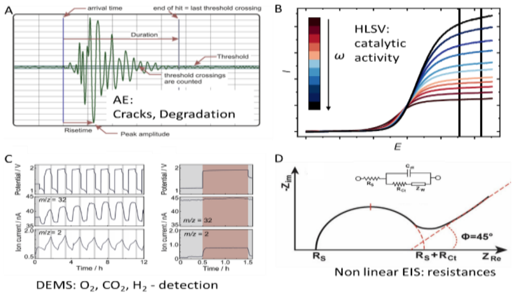

Figure 1: planned methods within the project.

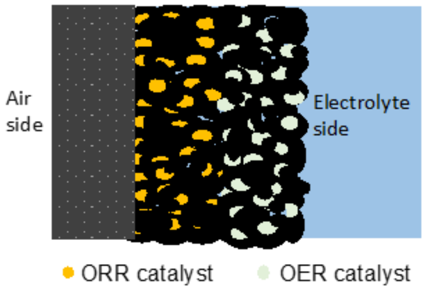

Figure 2: Scheme of bifunctional GDE.

Keywords*:* Zinc-Air Battery, bifunctional catalyst, GDE.

1. . Arai, H.; Garche, J.; et al. *"Metal–Air Batteries: Present and Perspectives",* **2020**, *1*, ISBN: 9780444643346

Energy Storage System (ESS) using Zinc-Air Batteries

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The demand for energy storage is experiencing a significant surge due to the electrification of transportation and the expansion of renewable energy sources. Zinc-air batteries hold immense promise as an energy storage solution due to their high energy density and recyclability. However, their lower power density compared to lithium-ion cells and the challenging state estimation have so far limited their use in typical applications.To tackle this issue, this research project focuses on analyzing and optimizing the cell chemistry and geometry of zinc-air cells to increase their power density. The project goals, as illustrated in Figure 1, have been surpassed by leveraging 3D-printing technology for rapid prototyping of different cell geometries.

Rechargeable zinc-air cells have flat voltage characteristics, which makes state estimation challenging. To address this, a low-cost measuring system has been developed that measures electrochemical impedance spectra. This system is specially adapted to zinc-air cells and can be used to measure impedance spectra during operation for cells with 3 electrodes. By combining this system with machine learning algorithms, it is possible to determine the state of charge accurately. A test system has been set up at the Stadtwerke Steinfurt 100kW peak PV system. The demonstrator is assembled in a standard server cabinet, with 6 battery stacks of 12 cells each, as shown in Figure 2. In total, this results in 72 cells and a capacity of 7.2 kWh. All stacks are connected to the control unit via CAN bus, which enables the entire demonstrator to be managed. The control unit can switch individual stacks between charging and discharging, depending on the available PV power.

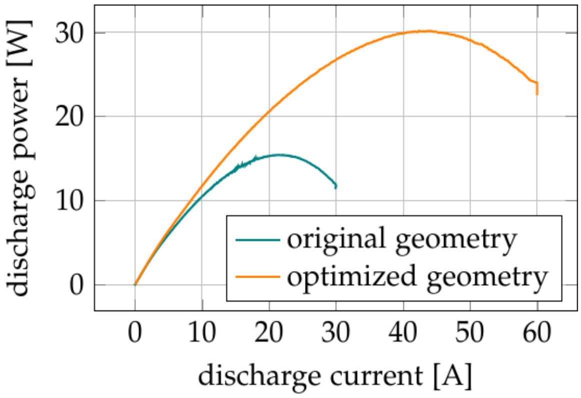

Figure 1: Discharge power as a function of the discharge current of a power-optimized zinc-air cell

Figure 2: Zn-Air Battery Stack

Keywords: zinc-air battery, energy storage system, battery management system

1. A. Loechte, I.R. Ruiz, P. Gloesekoetter, Battery State Estimation with ANN and SVR Evaluating Electrochemical Impedance Spectra Generalizing DC Currents, Applied Sciences, 12(1), p. 275, 2021, DOI: 10.3390/app12010274

Improved Electrochemical Performance of Zinc Anodes by Electrolyte Additives in Near-Neutral Zinc-Air Batteries

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Metal-air batteries are considered up-and-coming electrochemical energy storage technologies due to possessing very high theoretical energy densities while utilizing cost-effective, safe, and abundant materials. Among various possible configurations, zinc-based metal-air batteries are one of the most advanced for primary and secondary applications. Although primary Zinc-air batteries (ZABs) have been commercially available for various applications, secondary batteries have faced challenges, especially in alkaline media. In this regard, employing aqueous neutral electrolytes brings several advantages, such as suppressed carbonization of the electrolyte and dendrite formation. However, the performance of such ZABs with neutral electrolytes can be hindered by the passivation of the zinc surface, the formation of insoluble zinc species, and corrosion.

The objective of the present work is to evaluate the influence of Ethylenediaminetetraacetic acid (EDTA) electrolyte additive on the performance of near-neutral secondary Zn-air batteries. The electrochemical behaviour of Zn electrodes was investigated in 2M NaCl (pH 10) solutions with and without EDTA additive. Initially, open-circuit and potentiodynamic polarization experiments were conducted to extract the corrosion parameters of the Zn electrodes. The intermediate-term (24 h) discharge experiments were performed under current densities of 0.1, 0.25, 0.5, and 1 mA/cm^2 in a three-electrode half-cell setup. These electrochemical measurements confirmed that Zn is only partially active in neat 2M NaCl electrolytes. However, it could still be discharged up to 1 mA/cm^2 at discharge potentials around −1.0 $V_{Ag/AgCl}$. In order to study the dissolution behaviour and the discharge products, the surface of the electrodes was further characterized by a laser scanning microscope (LSM), X-ray diffraction (XRD), and scanning electron microscope (SEM) upon discharge experiments. The performance of full-cell Zn-air batteries was then evaluated in galvanostatic discharge experiments (in primary-mode) up to 930 h with specific energies up to 840 Wh/kg$_{Zn}$ and in galvanostatic cycling experiments (in secondary mode) up to 575 h with 70 cycles. In comparison to neat electrolytes, the addition of EDTA to the electrolyte results in enhanced specific energies and mass utilization efficiencies of near-neutral zinc-air batteries.

***Keywords**:* Zinc-air battery, neutral aqueous electrolyte, additive, EDTA

Developing a recyclable, rechargeable stationary zinc-air cell – ZinCycle

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Driven by the by the demand for safe and environmentally friendly energy storage solutions for fluctuating renewable energy, zinc air cells have received revived interest as one of the proposed post lithium-ion technologies. In recent years, many solutions for the various problems of rechargeable zinc-air cells have been published in literature. Here we want to present the project ZinCycle, funded by the German federal ministry for education and research, which aims to develop a new zinc-air battery stack for stationary applications, using new ways to overcome the main problems of zinc-air cells.

While there are numerous publications on new air electrodes and ways to prevent dendrite formation, hardly anyone considers the cell assembly or the bipolar plates. In this project, the assembly of the zinc-air cells should be simplified by using membrane-separator-units, developed by our partners Westfälische Hochschule and Rhenotherm.

The dendrite problem should be solved by the University of Bayreuth by covering the zinc particles supplied by Grillo-Werke AG in conductive glass. This glass not only traps the oxidation products and therefore prevents shape change and dendrites, it also hinders passivation and forms a conducting network in the discharged cell [1].

Another part of zinc-air cells usually forgotten in literature is the bipolar plate. In this project, Eisenhuth GmbH aims to develop a carbon-metal-compound material which is chemically stable, has a low contact and electric resistance and is moldable as well.

Although everyone claims that zinc-air batteries are environmentally friendly, hardly any group considers the environmental impact of their cell components beside zinc or the recycling of these components. Currently, the recycled components are of poorer quality than the ones used for the construction of these cells [2]. Our partner Accurec aims to change that and obtain battery grade materials after recycling. In this project, the EURA AG continuously monitors the environmental impact of all battery components to minimize the footprint of the whole cell.

VARTA Microbattery GmbH and the University Duisburg-Essen will put all these parts together and build a battery stack with a peak power of 100 W and a capacity of 100 mAh.

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Alder charcoal-based materials as oxygen reduction catalysts for primary Zinc-Air Batteries

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A strategy to fulfil the need to increase the sustainability of the present energy resources and replace fossil fuels is the deployment and use of woody biomass as a raw material for energy applications. The goal of this research is to synthesize a functional material using alder charcoal as a raw material via thermochemical activation with NaOH and subsequent nitrogen and metal (Co, Zn, Cd, Mn, Ni) co-doping.

After thermal activation and co-doping, the electrochemical performance of the alder charcoal-based samples was assessed. The as-prepared co-doped carbons have shown good activity towards oxygen reduction reaction (ORR), with the onset and half-wave potentials of approximately 0.85–0.90 and 0.80–0.85 V, respectively, showing the four electrons transfer path in 0.1 M KOH solution. Consequently, these materials are representing a promising alternative to conventional electrocatalysts for energy applications in alkaline electrolyte systems such as primary zinc-air batteries (ZAB).

ORR gas diffusion electrodes based on the alternative co-doped carbons were fabricated and tested as the cathode in primary ZAB. Discharge and specific capacity profiles at different current densities and the corresponding power densities will be presented and compared with the state-of-the-art MnO_2/carbon mixture.

This work has received funding from the Baltic Research Programme project “Sustainably produced nanomaterials for energy applications (SuNaMa)” (No. S-BMT-21-12, LT08-2-LMT-K-01-055).

***Keywords**:* zinc-air batteries, carbon, doping, alder charcoal, oxygen reduction

Bifunctional Zn-air battery gas-diffusion electrodes: a study centered on X-ray absorption microspectroscopy

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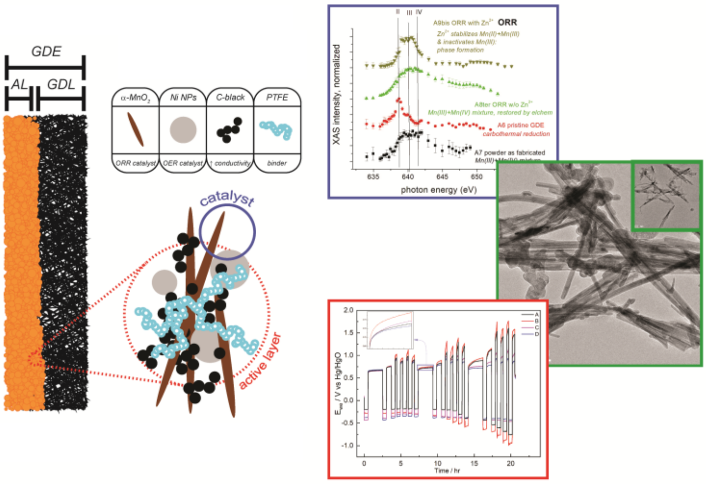
This work is centered on the fabrication of a novel gas diffusion electrode (GDE) and on its electrochemical, structural and compositional characterization, in view of the assessment of the physico-chemical factors impacting its efficiency and durability in operating ambient[1]. The ORR and OER electrocatalysts were α-MnO_2 nanowire and Ni/NiO nanoparticles, respectively[2]. The GDEs were fabricated by spray-coating a water-based catalyst ink, with added PTFE and C-black, onto C-paper. Different Ni/NiO nanoparticle contents were considered, to evaluate the effect of the OER catalyst on electrochemical performance and durability of the bifunctional GDE. Pure electrocatalysts and GDEs, in pristine state and after ageing under operating conditions, were characterized with direct- and Fourier-space spectromicroscopy at the Mn, Ni and Zn L-edges, complemented by SEM microscopy and HRTEM. This multi-technique approach enabled molecular-level understanding of the performance and degradation of bifunctional ORR/OER electrocatalysts, in the realistic GDE context. In particular, the drift of the ORR electrocatalyst chemical state of Mn away from the optimal 3+/4+ mixed valence state as a result of ageing and Zn^{2+} contamination, was followed and correlated with electrochemical conditions, as well as with crystal structure evolution[3].



***Keywords**: gas-diffusion electrode, X-ray absorption, microspectroscopy, degradation*

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Model based insights into the performance of zinc manganese dioxide batteries in the presence of pH stabilization substances

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Rechargeable aqueous zinc manganese dioxide batteries (ZMB) show some promising characteristics with respect to stationary storage applications. They are low cost, safe, environmentally friendly, and use readily available materials that are degradable in Europe. Therefore, the research field has received much attention in recent years to solve the existing challenges for global use. Thereby the mechanism at the positive electrode is still under strong debate. The accessibility of the Mn2+/Mn4+ deposition mechanism at the positive electrode is promising in terms of increasing the energy density due to the two-electron mechanism and the higher voltage potential. Operation in the acidic pH range, which provides sufficient protons, however, leads to severe stability problems of the zinc anode, which results in corrosion and hydrogen evolution [1]. A different approach is taken by Mateos et al. who demonstrate that the two-electron mechanism can be accessible even under mild non-corrosive conditions by creating a local proton environment through the addition of buffer substances [2]. This principle has been confirmed from different groups but still, it is a more detailed understanding needed of how the systems work under these complex conditions. Therefore, a comprehensive mathematical model is developed, that can represent the complex homogeneous reactions within the electrolyte and therefore also allows the addition of different buffer substances to stabilize the pH and their influence on cell performance to be investigated. This work could therefore be of great use to designing an efficient, long-life systems.

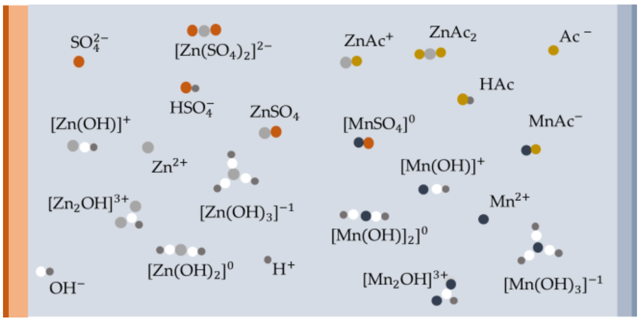

Figure 1: Complex speciation of the aqueous electrolyte from zinc manganese dioxide batteries

Keywords: zinc manganese dioxide battery, buffer, battery modeling

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Zinc Battery “ABBy” as a next Generation Battery for Stationary Storage System

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This work examines the challenges faced by the cathode's lifespan and dendrite formation on the anode, as well as corrosion on the anode in zinc batteries. HILABS investigates whether zinc-air batteries or zinc-ion batteries can solve these issues. Zinc-air batteries have a lower overall efficiency of about 45-50% in practice, while zinc-ion batteries have a much higher efficiency of 85-90%. The problem of zinc corrosion and dendrite formation is addressed by using an ion-conducting membrane, developed by HILABS. This not only prevents dendrites from growing through the cell and causing short circuits, but also prevents water from the electrolyte from reaching the anode and causing corrosion. A carbon-based material with 3D structure and high capacity and durability was developed as the cathode. As a result, HILABS has developed a cell with several thousand cycles and high efficiency, making it possible to build stationary power storage systems with energy density up to 50 Wh/L and 30Wh/kg for households and industry storage. A pilot project has been initiated.

Figure 1: Battery Cell ABBy

Figure 2**:** 5 kWh Zinc Battery System

Keywords*:* Zinc-Air and Zinc-Ion-Battery, Carbon Electrode

AMAZE: Advanced Manufacturing of Zn Electrodes for Rechargeable Zn-air Batteries

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The development of electrically rechargeable zinc-air batteries (ZAB) has been frustrated by the limited reversibility of the zinc-based electrode. Extensive research carried out over the last decade on the ZAB cell components such as bi-functional catalysts, electrolyte additives, and electrode structures has resulted in an improved cell-level specific power at laboratory scale. However, transferring academic success towards feasible realization is still a challenge majorly due to shortcomings with upscaling, manufacturability, and the pertinent economic benefits.

The AMAZE project, a joint effort from academia (IZTECH, Turkey), a research institute (SINTEF, Norway), and industry/SME (EASYL, France), aims to develop scalable and techno-economically viable methods for the manufacturing of porous Zn electrodes and thus, to contribute to the development of the next generation of rechargeable ZABs. Through a two-pronged approach, and by applying 3D printing for the copper current collectors, AMAZE will deliver a new generation of thick, porous Zn electrodes with an optimal pore structure for high performance and extended cycle life through better Zn utilization, electrochemical performance, and structural stability. To that end, the AMAZE consortium will develop scalable cost-competitive porous Zn electrodes through i) calcium zincate-based 3-D structures through a low-temperature dry mix technology and ii) zinc-based 3-D structures through additive manufacturing (AM) technology. In addition, in combination with the 3D printing Cu current collector architecture, other methods of manufacturing Zn electrodes such as cold sintering and Zn paste would be explored. The two methods selected for Zn electrode manufacturing have a high potential for upscaling, which is vital for the industry-scale production of ZABs in the near future. An environmental and life cycle costing analysis of the two approaches will be made to create a viable plan for future developments.

Keywords*:* zinc-air batteries, additive manufacturing, calcium zincate, current collector, cold sintering

Segmented current collector technology and their application on Zn-air batteries

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One of the major drawbacks of renewable energy production and use is that efficient energy storage is required, due to the intermittent nature of wind and solar power.

Zinc based metal-air batteries have the advantage of high energy density, because oxygen from ambient air is used without in-cell storage. As a consequence, lighter batteries are produced with the reversible available Zinc as the only limiting factor.

However, before Zn-air batteries can be used as secondary elements some obstacles have to be overcome. The low cyclability of state-of-the-art Zn-air batteries is caused by the passivation rate and dendrite growth of zinc, carbonate formation in the alkaline electrolytes, corrosion of cathode materials and flooding of the cathode. All these factors are reason for heterogeneous current distribution which impacts the cycle life. This gets even worse if industrial relevant sizes of batteries are built.

Herein, we want to introduce the so-called segmented cell technique which is based on printed circuit-board technology and the use of segmented current collectors. This technique allows locally-resolved electrochemical measurements and can be performed during cell operation. This gives information about the current distribution which is otherwise only accessible through modelling approach.

We used a silver-based cathode with these segmented current collectors to investigate the influence of gas pressure and distribution as well as the interaction between both electrodes.[1]

In a second investigation we linked the hydrostatic pressure with the heterogeneous current distribution of the cathode by using pressure saturation curves, a hydrostatic pressure cell and the segmented current collector technique.[2]

The obtained knowledge enables a deeper understanding and shows the path for further research especially for larger cells.

Keywords*:* Full-Cell, segmented current collector, electrolyte saturation.

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Deciphering the cycling mechanism of manganese-oxide cathodes in zinc-ion batteries in near-neutral electrolytes: A theory based approach

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Zinc-ion batteries (ZIB) rely on a lithium-ion-like Zn^{2+}-shuttle, which allows higher roundtrip efficiencies and better cycle life than most other zinc-based chemistries. The most promising and best-studied candidates for zinc-ion batteries are manganese-oxide (MnO_2) cathodes. [1] ZIBs with aqueous neutral zinc sulfate ($ZnSO_4$) electrolytes exhibit two distinct phases during charge and discharge. Experiments have revealed that the second discharge phase goes hand-in-hand with the precipitation of zinc-hydroxide sulfate (ZHS) at the cathode.[2] Besides the most desired zinc insertion, the proposed working mechanisms of the MnO_2 cathodes are the (co-)-insertion of protons into the cathode and the reversible dissolution of the MnO_2 itself, both having similar effects on the local pH evolution eventually leading to ZHS precipitation. Recently, the close interaction of cathode dissolution and the formation of ZHS was shown experimentally.[2–4] Empirically, higher cycling stability was achieved by electrolyte additives, such as $MnSO_4$, but most of the work does not focus on the close interaction of the electrolytes pH and the cathodic reaction dynamics. Most importantly, a complete and consistent understanding of the two-phase charge and discharge mechanisms of such ZIBs is still lacking.

Our work uses a continuum full-cell model supported by DFT calculation to investigate the implications and details of the experimentally observed properties and deduced claims. We integrate the complex formation reactions in near-neutral aqueous electrolytes into a continuum 1D+1D battery model. We combine this approach with DFT calculations of the cathode structure with inserted zinc and proton to give a detailed picture of ZIB's cycling behaviour. We investigate the interaction of the cathodic proton reactions and the electrolyte's stability and precipitation characteristics in full-cell simulations. This helps us to identify the details of the charge-storage mechanism. We validate our model with experiments by comparing it with cell voltages during galvanostatic discharge and cyclometric voltammograms. Subsequently, we use this model to identify how the cycling behaviour is impacted by cell design and electrolyte composition and discuss optimizations of the interplay of cathodic dissolution and precipitation of ZHS.

***Keywords**: zinc-ion battery, battery, aqueous electrolyte, near-neutral electrolytes, manganese oxide*

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(4) Chen, H.; Dai, C.; Xiao, F.; Yang, Q.; Cai, S.; Xu, M.; Fan, H. J.; Bao, S. *Advanced Materials* **2022**, 2109092. https://doi.org/10.1002/adma.202109092.

Addressing the Voltage and Energy Fading of Al-air Batteries to Enable Seasonal/Annual Energy Storage

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The European Commission's Strategic Energy Technology Plan (SET Plan-2018) aims to slow down anthropogenic global warming by 2030 and is seen as a crucial intermediate step to guarantee net-zero greenhouse gas emissions by 2050. Its achievement requires a significant increase in renewable energy. Various technologies have been proposed to solve this issue, including power-to-X options, i.e., converting renewable electricity into a storable form (e.g., hydrogen), and secondary-battery-based power-to-power options.[1] Nonetheless, seasonal and even annual energy storage in a low-cost manner is still a challenge. In this context, employing the earth-abundant, low-cost, and easy to transport and store Al metal as the energy carrier may offer some valuable options, e.g., the combination of Al production via inert-electrode smelting (power to metal) and Al conversion to electricity via Al-air batteries (AABs, metal to power).[2] However, voltage decay during discharge severely decreases the practical energy density of AABs, especially, upon long-term operation.[3,4,5]
Herein, the electrochemical behavior of AMA in KOH aqueous solutions containing various concentrations of dissolved aluminum, predominantly present as $\mathrm{Al(OH)_4^-}$, is compared to investigate the impact of $\mathrm{Al(OH)_4^-}$.[6] It is observed that an increasing polarization of AMAs occurs even before any precipitate is generated on their surface. Further experimental and computational results reveal that the accumulation of $\mathrm{Al(OH)_4^-}$ greatly reduces the OH^- concentration and, in turn, negatively affects the reaction kinetics. Therefore, the voltage decay issue of AABs is caused by the accumulation of $\mathrm{Al(OH)_4^-}$ in the electrolyte rather than $Al(OH)_3$ on AMAs. Subsequently, it is demonstrated that seeded precipitation of $\mathrm{Al(OH)_4^-}$ in the electrolytes to $Al(OH)_3$ precipitate with releasing OH^- via utilizing its lower solubility at 20 °C than at 50 °C allows effective recovery of the potential of AMAs and the voltage of AABs. At last, prototype AABs are assembled and tested to evaluate the feasibility of voltage recovery via the proposed seeded precipitation process.

***Keywords**:* Al-air batteries, Seasonal/annual energy storage, Voltage decay, Aluminate, Seeded precipitation process

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Experimental evaluation of the main processes used for the simulation of zinc-air cells

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Recently, zinc-air batteries have received revived interest as one of the proposed post lithium- ion technologies. This revival is driven by the demand for safe and environmentally friendly energy storage solutions for fluctuating renewable energy. These energy storage systems need to address variable power, capacity and profitability requests. Zinc-air-flow batteries with high specific energy density, low-cost, highly available and eco-friendly active materials are suitable to fulfill these requirements. The use of a flow battery type with zinc-particles suspended in an alkaline solution (zinc-slurry) is uncommon but offers several distinctive insights to the processes inside the battery. In stationary cells, these insights are usually limited to cell voltage, impedance studies, sometimes the potential of the zinc electrode and post-mortem analysis. This data is sufficient to simulate the voltage curve of a commercial zinc-air button cell [1], but this simulation is based on a lot of assumptions which are impossible to prove with the available data. But to really understand the passivation mechanism and cell behaviour, more information is needed.

Fortunately, according to literature, the reaction mechanism of zinc is relatively simple and can be described by a modified Butler-Volmer approach. As zincate is the dominant species in solution, the concentration of OH^--ions can be calculated from the zincate concentration [1]. But as it is impossible to measure this concentration directly at the zinc surface, or to determine the starting point of ZnO precipitation, in the opaque slurry, these values are usually assumed.

In our flow cell, the residence time of the slurry is short enough to provide negligible discharge gradients. It is therefore possible to take samples, which properly analyzed, allow us to determine the zincate concentration and the starting point of ZnO precipitation. The active area of the zinc electrode is more difficult to determine, as not all zinc particles are active, but scanning electron microscopy and BET-measurements (supplied by Grillo-Werke AG) can show us the trends. This data put together with the simulations described in literature offers unique insights in the discharge process of zinc-air cells.

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$CoFe_2O_4$@N-CNHs: A bifunctional catalyst for rechargeable zinc-air batteries

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Highly efficient bifunctional electrocatalysts are one of the current challenges to accomplish long-standing rechargeable zinc-air batteries. Improving their performance has been recognized as key to developing better air batteries.[1] Among the non-precious noble-metal-free catalysts, transition-metal oxides have shown promising performances. Attempts to develop hybrid catalysts based on conducting frameworks e.g. composed of carbon and transition metal oxide materials as active components in the ORR and OER reaction, have contributed significantly to an advanced understanding in the field.[2] Even though $CoFe_2O_4$ has been reported in earlier studies as a bifunctional electrocatalyst,[3] $CoFe_2O_4$ nanoparticles decorated on nitrogen doped carbon nanohorns $CoFe_2O_4$@N-CNHs, as high performance materials in air cathodes have not been reported to the best of our knowledge. The herein reported $CoFe_2O_4$@N-CNHs composite catalyst was prepared using stoichiometric amounts of single source molecular cobalt and iron precursors and CNHs, in a NH_3 atmosphere, in a one-step process. This procedure is unique because it simultaneously leads to $CoFe_2O_4$ preparation and nitrogen functionalization of CNHs. The composite $CoFe_2O_4$@N-CNHs show better ORR and OER activity as compared to a composite of individual $CoFe_2O_4$ nanoparticles and CNHs. It exhibits full rechargeability and a high discharge capacity of 280 mAh/g at a lower current density.

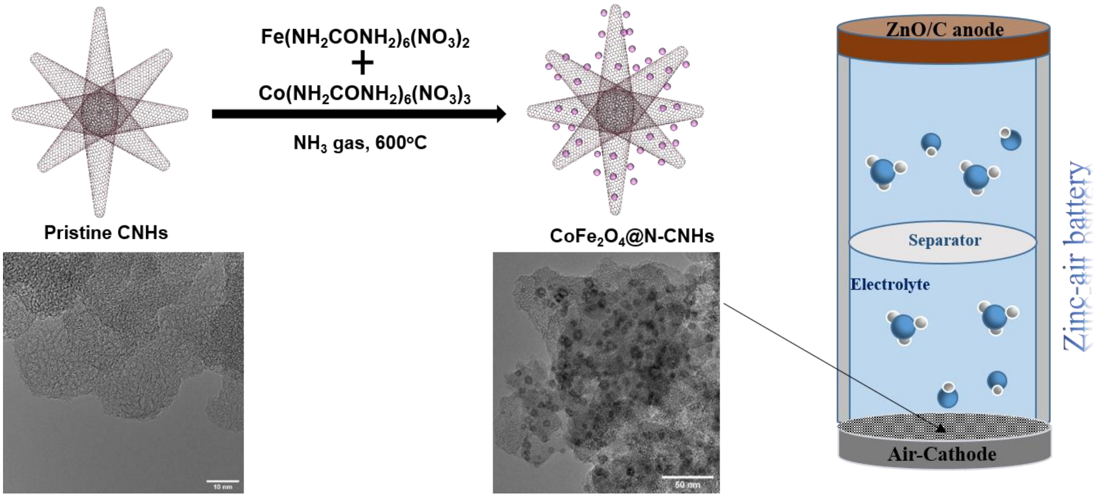

Figure 1: Scheme of synthesis of $CoFe_2O_4$@N-CNHs

***Keywords**:* $CoFe_2O_4$@N-CNHs, Bifunctional catalyst, Zinc-air battery.

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Development of a rechargeable jelly roll zinc/manganese battery

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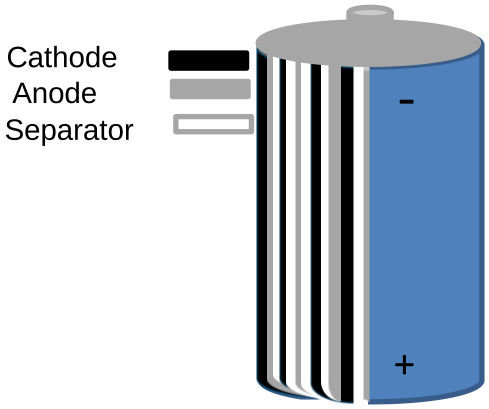
The project ***ZiMaBat*** aims at developing a rechargeable zinc manganese battery (ZMB) - also known as zinc ion battery (ZIB) - with a pH neutral or mildly acidic aqueous zinc sulphate electrolyte for stationary/portable applications. This battery is a safe, easy to recycle electrochemical storage system that relies on abundant raw material sources. Most important challenges are related to corrosive electrolyte properties, dendrite growth, hydrogen evolution as well as high self-discharge rate.

DECHEMA-Forschungsinstitut (DFI) main tasks focuses on the synthesis of large batch of δ-MnO_2 intercalation material for partners (e.g. Varta Consumer Batteries) and development of jelly roll type cell design. Therefore, different Zn foils/powders from partner Grillo, current collectors and binders for δ-MnO_2 cathode, as well as separators have been tested. Some preliminary results on material selection as well as performance of the best cells will be presented.



Schematic component arrangement for the ZMB jelly roll AA cell design at DFI

Keywords*:* δ-MnO2, ZMB battery, AA cylindrical cell

Model-based Voltage Response Prediction for a Primary Zinc-Air Cell

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Good models are key for the design of control systems, monitoring mechanisms, optimal operation, and, more specifically, for Battery Management Systems. Our ongoing research aims to build a model-based mechanism to predict the output voltage of a primary zinc-air cell as a function of the operating current, which may not be constant for the entire discharge cycle. This process faces multiple difficulties: first, the cell exposes a nonlinear steady-state voltage response, which is influenced by the cell's physical construction, and second, the time constant of the step response is a nonlinear function of the current. Our approach goes further than previous models, as it exploits a piecewise current input to identify the parameters in both steady state and transient response. The results we present are accompanied by the data treatment and model construction, which is compared to previous approaches and real data.

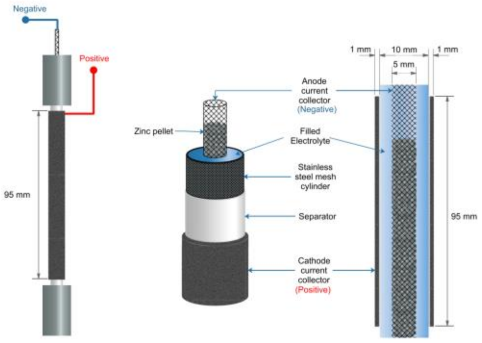

Figure 1: Zinc-air cell

***Keywords**:* Parameter identification, Energy Storage, Dynamical model of cells.

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The Organic/Inorganic Composite Separator for Rechargeable Zinc Batteries

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In recent years, demand for high-performance, low-cost electrochemical energy storage devices has increased, and Zn-based batteries using Zn metal as active material have attracted widespread attention due to their inherent advantages. However, it is also generally recognised that rechargeable zinc batteries have some significant drawbacks. The problem of dendrite growth is one of them and remains unsolved in zinc rechargeable batteries. In order to improve the cycle life of rechargeable zinc batteries, we have developed an organic/inorganic composite separator that exhibits an inhibitory effect on short circuits caused by zinc dendrite growth. This separator is designed to have a sufficient ionic conductivity as well as suppression properties for preventing a short circuit. To obtain these performances, inorganic particles and hydrophobic particles are utilized which provide no extra space and no extra electrolyte for dendrite growth. The developed separator was also found to have a longer life in nickel-zinc battery systems. As a result, the cycle life of the organic/inorganic composite separator is more than ten times longer than that of conventional microporous membranes. Furthermore, the separator is expected to be effective not only in improving the life of nickel-zinc batteries, but also in improving the life of rechargeable zinc batteries such as zinc-air batteries, which suffer from similar problems.

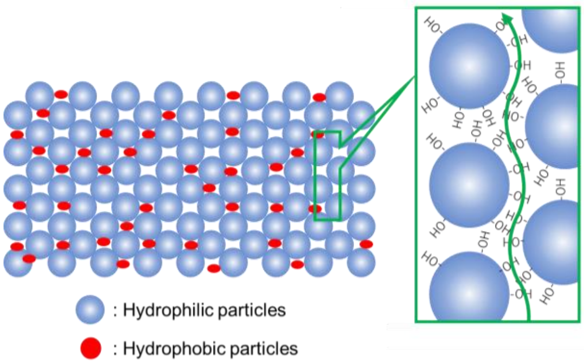

Figure 1: A schematic diagram of the separator. It is mainly formed by the hydrophilic particles.

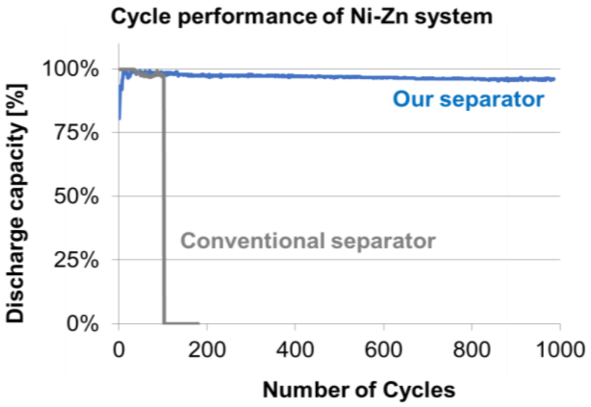

Figure 2**:** The results of the cycling properties. It shows discharge efficiency of the Ni-Zn battery.

Keywords*:* rechargeable zinc battery, zinc-air battery, separator, dendrite.

1. S. Ogawa. et al. *Electrochemistry* **2022**, 90 (1), 017001. DOI: 10.5796/electrochemistry.21-00099

Ni–Zn Stacked Battery with Organic/Inorganic Separator.

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As the demand for electrochemical energy storage devices has increased, there is a need for secondary batteries. As one of them, Zn-based batteries have attracted attention due to high-efficiency, safety, low-price, and environmental friendliness. However, Zn-based batteries have a limited poor cycle life. The causes of these problems are shape change, densification, and internal short-circuit. The biggest problem of all is the short-circuit caused by dendrite growth. In order to improve the cycle life of Zn-based battery, we have developed an organic/inorganic composite separator. This separator exhibits high short-circuit resistance in a test battery cell having a nickel positive/zinc negative electrode pair parallel structure. However, in order to improve reliability, it is necessary to evaluate it with an actual battery. In this poster session, we report evaluation results of a stacked nickel-zinc battery intended for an actual battery and that our developed separator can effectively suppress short-circuit caused by zinc dendrite even in this stacked nickel-zinc battery.

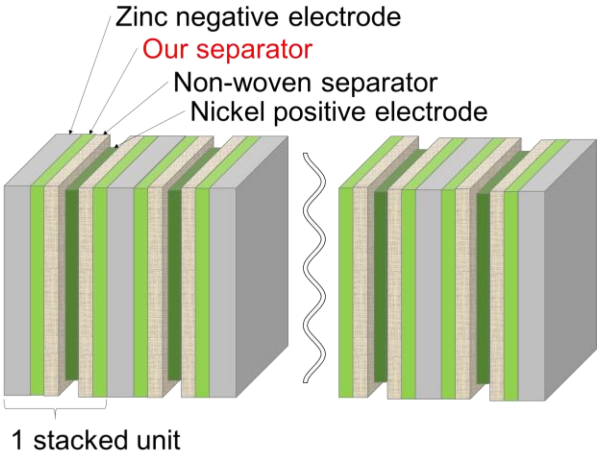

Figure 1: Schematic diagram of Ni-Zn stacked battery with organic/inorganic separators.

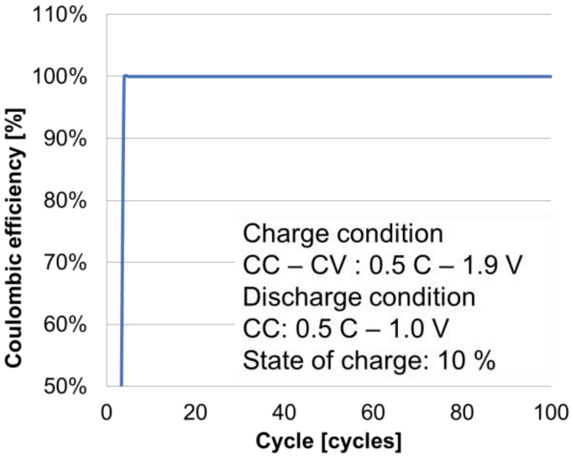

Figure 2**:** Cycle performance result of stacked Ni-Zn battery with organic/inorganic separators.

Keywords*:* separator, rechargeable zinc battery, Ni-Zn battery, dendrite.

1. S. Ogawa. et al. *Electrochemistry* **2022**, 90 (1), 017001. DOI: 10.5796/electrochemistry.21-00099

Understanding H_2 evolution electrochemistry to minimize solvated water impact on zinc anode performance

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H_2 evolution is the reason for poor reversibility and limited cycle stability of Zn metal anodes and impedes practical application in aqueous zinc ion batteries (AZIBs). The H_2 evolution potential in zinc ion electrolyte is not reliably known. Thermodynamically, zinc metal is unstable during charge/discharge because the theoretical Zn^{2+}/Zn redox potential of -0.76 V vs SHE is more negative than that for H_2 evolution of -0.41 V vs SHE, at pH = 7.[1,2] Nevertheless, the high over-potential of H_2 evolution on zinc metal could practically move H_2 evolution to a more-negative potential. We evidence, using linear sweep voltammetry (LSV) in mild electrolytes (1, 5 m NaCl and 1, 5, 10, 20 and 30 m $ZnCl_2$) that H_2 evolution occurs at a more negative potential (-1.34 V vs. SCE) than zinc reduction (-1.05 V vs. SCE) because of high overpotential against H_2 evolution on Zn metal. Glycine additive is also used to reduce solvated water and to suppress H_2 evolution as well as other ‘parasitic’ side reactions on the Zn anode. We evidence that this electrolyte additive suppresses H_2 evolution and reduces corrosion in Zn|Zn and Zn|Cu cells when compared with bare $ZnSO_4$ electrolyte. We demonstrate Zn|PANI (highly conductive polyaniline) full cells exhibit excellent electrochemical performance in 1 M $ZnSO_4$-3 M glycine electrolyte and a high reversible capacity of 100 mAh g^{-1} in a practical Zn|PANI pouch cell. We conclude that this new understanding of electrochemistry of H_2 evolution can be used to design relatively low-cost and safe AZIBs for practical large-scale energy storage.

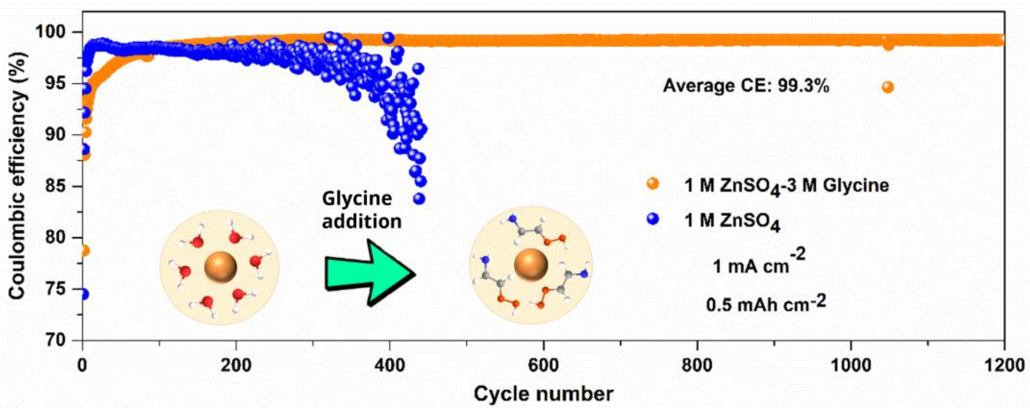

Figure 1: Coulombic efficiency (CE) of Zn plating/stripping on Cu in different electrolytes.

***Keywords**:* zinc-ion battery, H_2 evolution, aqueous electrolyte.

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ZABAT: Advancing Sustainable Energy Storage through Rechargeable Zn-Air Batteries for the European Green Deal

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The ZABAT project aims to support the European Green Deal by developing and validating a new eco-friendly, high-performance rechargeable Zn-Air battery (r-ZAB) with a focus on behind-the-meter energy storage applications for industry and households coupled with renewables. This battery technology will play a crucial role in achieving the mid- and long-term EU climate and energy goals by enhancing the stability and security of Europe's energy supply. In addition, this approach aligns with the United Nations' sustainable development goals, promoting a circular economy and sustainable energy storage practices.

The primary objective of ZABAT is to create a critical material-free energy storage system based on abundant zinc (Zn), which will significantly reduce the reliance on critical raw materials (CRMs) like lithium and cobalt. To achieve this goal, ZABAT will address key challenges in Zn-Air battery technology. The project will focus on several specific objectives (SOs), including developing porous Zn electrodes with high utilization and cycle life, formulating (hydro)gel electrolytes based on semi-interpenetrating polymer networks (semi-IPNs), and creating 3-dimensional bifunctional electrodes with non-precious CRM-free catalysts. Parallel to this, through sustainable and circularity assessments, ZABAT will also focus on addressing environmental, toxicity, and societal impacts related to the materials and processes employed in the r-ZAB technology.

The ZABAT project involves an interdisciplinary RD&I team comprising five partners from four countries. This includes a university with expertise in graphene-based materials synthesis and characterization, three European research organizations with a strong background in electrochemical energy storage technologies, and an industry partner with extensive experience in developing 3D structured carbon for energy storage applications. Moreover, the project will involve various industry stakeholders, including GDE manufacturers, electrolyte manufacturers, material manufacturers, cell manufacturers, and recyclers as an industrial advisory board to ensure the practicality and industrial relevance of the developments.

The main outcome of the ZABAT project will be the development of a prototype cell with a capacity of 1Ah and improved performance and long-term cycling capabilities. Besides this, project's outcomes will significantly advance Zn-Air battery technology, offering a cost-effective and eco-friendly energy storage solution that can support the integration of renewable energy sources into the EU grid and contribute to a sustainable energy future.

***Keywords**:* Energy Storage Technologies, Zn-Air Battery, Sustainable Development, Circular Economy

Preparation of rechargeable Zn electrodes by the Cold-Sintering Process

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The objective of this work is the preparation of porous Zn electrodes with high areal and mass loading for rechargeable batteries using the Cold-Sintering-Process (CSP), simple and cost-effective method. The CSP offers the advantage of tailoring electrodes with adjustable mass and areal loading, making it a promising approach for battery applications.
The starting material consists of a mixture of ZnO and dendritic copper, densified at room temperature. In the activation step, ZnO in the electrode is electrochemically reduced to Zn, creating voids and forming a porous electrode.
The conductive porous matrix is provided by dendritic Cu, ensuring high electric conductivity throughout electrode operation. The choice of ZnO and dendritic Cu in appropriate ratios ensures the formation of a percolating matrix, maintaining high electric conductivity and acting as a physical barrier for zincate ions. The precipitation of zincate ions into these pores is favored during subsequent charge-discharge cycles, thus hindering the shape change of the electrode.

The produced electrodes exhibit an utilization of 90% when used in a primary battery with a current density of 19.2 mA·cm^{-2}. Additionally, the electrodes were cycled with a current density of 2.3 mA·cm^{-2} under stringent conditions in zincate-free 6M KOH without any membrane or additives that would suppress hydrogen evolution, passivation, dendrite formation, or shape change. With areal capacity of 77 mAh·cm^{-2}, the electrodes exhibit over 100 cycles with an average coulombic efficiency of around 90% at a D.O.D. of 10%.

The performance of these electrodes compares favorably to state-of-the-art Zn electrodes [1] highlighting the potential of the CSP method for a facile preparation of rechargeable Zn electrodes.

Keywords*: Porous Zinc electrodes, Cold-Sintering-Process (CSP), rechargeable batteries*.

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Investigating the Influence of Cationic Species on Zincate Ion Diffusion in Highly Alkaline Electrolytes

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Rechargeable alkaline zinc-manganese dioxide batteries (ZMBs) have been identified as a promising technology for stationary energy storage due to their affordability, high energy density, safety, and material abundance. However, their rechargeability is impeded by Zn poisoning of the MnO_2 cathode during battery discharge, where zincate ions react with the Mn species, forming the irreversible phase hetareolite [1]. To address this challenge, we propose a separator capable of selectively blocking zincate ions, thereby mitigating their adverse impact on the MnO_2 cathode.

In this work, we build upon the methodology established by Duay et al. [2] to evaluate the zincate diffusion coefficients of various separators using anodic stripping voltammetry (ASV). We conducted measurements on a rotating disk electrode (RDE), achieving a detection limit for zincate ions within the sub-ppm range. Our investigation revealed that the diffusion coefficients of zincate ions through the Celgard 3401 separator varied depending on the cationic species (NaOH vs. KOH) and concentration (6 M vs 10 M). Interestingly, these diffusion coefficients diverged from those measured in the bulk electrolyte, despite the Celgard 3401's pores exceeding several nanometers in size.

To investigate the role of both the separator and the cationic species on the zincate ions' diffusion coefficient, we assessed zincate diffusion in the bulk electrolyte using another RDE technique proposed by Pessine et al. [3]. This method correlates the diffusion limiting current with the zincate diffusion coefficient. We subsequently employed the Stokes-Einstein equation to estimate the solvodynamic radius of the zincate ion in these electrolytes.

Our findings demonstrate a significant dependence of the solvodynamic radius of the zincate ion on the electrolyte's cationic species and its concentration. These results suggest that the separator's selectivity - and, by extension, the lifetime of rechargeable ZMBs - is heavily influenced not only by the separator itself but also by the electrolyte composition selected.

***Keywords**:* Rechargeable alkaline zinc-manganese dioxide batteries, Separator, Rotating Disk Electrode

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Nanostructured Carbon-free Cathodes for Zinc-air Batteries

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The increasing demand for electrical energy storage needs to be accompanied by high-performance and cost-effective devices to accomplish European goals of 2050. In this scenario, interest for metal-air batteries is increasing since the air-breathing cathode configuration makes them more compact than conventional lithium-based batteries, resulting in a higher theoretical energy density.

Zinc-Air Batteries (ZABs) also present advantages such as environmental-friendliness, safety and affordability since zinc is an earth-abundant material and possess good stability and electrochemical reversibility in aqueous electrolyte [1].

Nevertheless, performance of this class of batteries is largely limited by the sluggish Oxygen Reduction Reaction (ORR) and Oxygen Evolution Reaction (OER) kinetics, resulting in small current density and large electrode polarization [2].

Moreover, the carbonaceous catalyst support is promptly deteriorated in the high-oxidative OER environment, leading to a mechanical collapse and therefore a severe reduction in electrode cyclability [3]. All these issues hinder the growth of ZABs respect Li-ion batteries in terms of performance and durability aspects.

In this perspective, our idea is to optimize a Transition Metal Oxide (TMO) electrocatalyst based on manganese oxide and to deposit it making a hierarchical structure directly onto a porous metallic substrate, which acts as current collector. Indeed, the aim is to tune the crystalline phase and the oxides composition to modify electronic structures, to optimize their catalytic activities and achieve performances comparable to those of benchmark materials, i.e., Pt/C for ORR and RuO_2, IrO_2 for OER [4].

***Keywords**: Zn-air batteries, electrocatalysis, manganese oxide, nanostructured cathode*

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A novel Zinc-Air Fuel Cell design: development and experimental characterization

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In the present work, a new fluidized-bed zinc-air fuel cell (ZAFC) was designed, developed, and experimentally characterized. The integration of the flowing electrolyte and zinc particles enables a fluidized-bed zinc-air fuel cell, which leads to fundamental advantages, such as the high surface area of the zinc particles, or the removal of reaction products from the proximity of the electrodes, reducing the concentration overpotential, due to the concentration gradient of the electrode species in the diffusion boundary layer between the electrode-electrolyte interface and the bulk of the electrolyte. In addition, as shown in Figure 1, the flowing electrolyte is useful for transporting zinc particles that have reduced in size due to the anodic reaction out of the cell: the initial size of these reduced zinc particles and the spent electrolyte are regenerated in an external electrolyte device.

The fluidized-bed ZAFC described in this work achieved a peak power density output of about 0.170 W/cm^2 corresponding to a current density of about 260 A/cm^2 and a cell voltage of 0.67 V under the best operating conditions. It should be noted that this performance was achieved by using atmospheric air at atmospheric pressure, thus without the use of a fan or compressed air or pure oxygen; this is an important observation because increasing the partial pressure of oxygen can improve its diffusion within the cell and consequently the oxygen reaction rate, which results in higher current and power density.

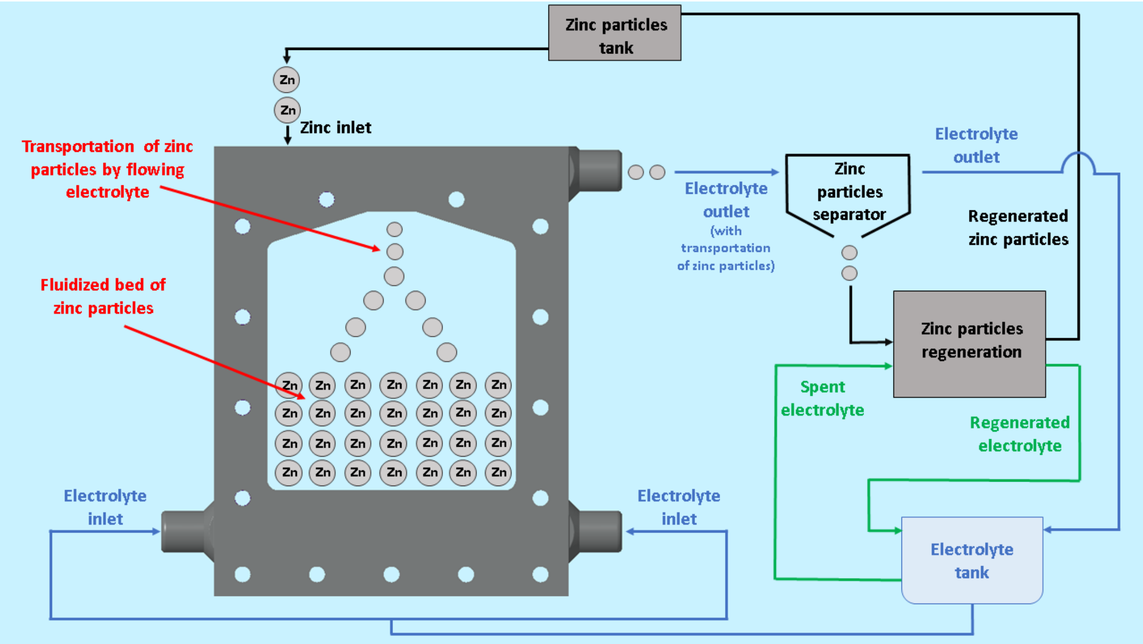

Figure 1: Zinc-air fluidized bed fuel cell, a regenerative setup

***Keywords**: Zinc-air, fuel cell, fluidized bed electrode.*

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