Effect of surfactants and wetting agents on the electrochemical characteristics of Ni/Zn batteries

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Nickel-zinc batteries are an attractive ecologically acceptable electrochemical system characterized mainly by good gravimetric energy density, high discharge acceptance, low cost and excellent safety. Historically, their unsatisfactory cycling stability largely due to electrode shape change, dendrite formation and zinc electrode corrosion are the major obstacles limiting their wider market penetration. In the present study we are investigating and optimizing some arrangement of the Zn active mass composition used as a negative electrode in these batteries. Through the use of various additives and some wetting agents, the substantial influence that the binders have on the performance of the zinc electrode is demonstrated. The use of surfactants, on one hand, reduces to some extent the resistance of the electrode, but on the other hand, increases its weight loss, consequently demonstrating a reduction of the operating cell life. Work in this direction is continuing using other pre-selected binders and surfactants on electrodes having larger size and/or cells configured with more electrode pairs. The use of gelled and/or membrane electrolytes may also lead as an additional barrier toward Zn dendrite formation and thus enhancing and prolong cell life.

Keywords: Ni/Zn batteries, surfactants, wetting agents

INTRODUCTION

With the progression and development of human society, the accelerated depletion of traditional energy sources and environmental pollution has become a focus of an extensive concern. Thus, the exploration of economic, environment friendly and reliable renewable energy sources is continuing to be a prevailing trend. Sustainable energy transitions require formulation of effective policies promoting and exploring biomass resources, increasing use of renewable and low carbon sources and discouraging the use of fossil fuels and unsustainable natural resources [1, 2].

In parallel, alternatively to this direction, a new look is taken on the development of a new generation of systems for accumulating and storing energy, as well as enhancing the existing ones. Table 1 compares some of the main electrochemical performances of different electrochemical sources we currently use. Among these power sources, lithium-ion batteries were deemed as one of the superior candidates due to their high output voltage and high energy densities [3, 4]. However, lithium-ion batteries are still insufficient for various applications because of the imminent safety problems such as short circuit due to Li dendrite formation and side reactions of $LiPF_6$ and organic carbonates under overcharge or high temperature. It is very difficult to achieve a fast-charging algorithm, related to the overheating of the system decreasing its safety behavior. High costs and harsh using conditions also put limits to its wide use in many particular applications.

On the other side, nickel-zinc (Ni/Zn) batteries are showing an increased research interest due to their impressive theoretical specific energy density ($\approx$372 Wh kg^{-1}), acceptable output voltage ($\approx$1.8 V), sufficient and inexpensive zinc resources, and low environmental concerns [6]. Manufacturing the nickel-zinc (Ni/Zn) battery is a promising technology for use in hybrid/electric vehicles and new portable devices. It delivers high specific energy (70–85 Wh kg^{-1}) and specific power (140–200 W kg^{-1}), and the operating cell voltage (1.6 V) is by 400 mV higher than that of Ni/Cd and Ni/MH batteries [7-9]. Definitely, they are an excellent choice for all of the stationary applications, where the low weight of Li batteries is losing its advantage. Nickel-zinc batteries play a significant role in consumer electronics applications such as digital cameras, portable lighting apparatus and cellular phones, because of their unique advantages like high output voltage and splendid power density [10]. Last but not least, it should be noted that Ni/Zn batteries can be almost completely recycled in the absence of residual pollutants and emissions, as shown in Figure 1 [11].

Table 1. Comparison of the main characteristics of different types of batteries [5]

| Parameter/Battery	Pb-Acid Flooded	PB-Acid TPPL	NiCd Pocket	NiMH	NiZn Prototype	Li-Ion
Nominal Cell Voltage, V	2.11	2.16	1.2	1.2	1.65	3.2-3.8
Gravimetric Energy, Whkg^{-1}	30-34	40-44	20-30	50-60	70-85	95-110
Volumetric Energy, WhL^{-1}			35-60	100-120	>135	
Gravimetric Peak Power (15 sec), Wkg^{-1}			20 – 75	>1000	>1000	
Volumetric Peak Power (15 sec), WL^{-1}			30-135	>1000	>1000	
High Current Discharge at low SOC	No	No	Partial	Partial	YES >5C	YES >2C
Operating Temperature, °C			-30 to +45	-20 to +40	-30 to+60	
Life @ 80% DOD; C/5			>500	800	>500	
Charge/Discharge Factor			>1.4	>1.25	<1.03	
Self-discharge, %/day	Moderate	Moderate	0.3-0.5	3 to 5	0.2-0.3	0.5-1.0
Recharge Time (> 80% SOC), h	8-10	8-10	2.5-3	1-2	0.5-1	1-2
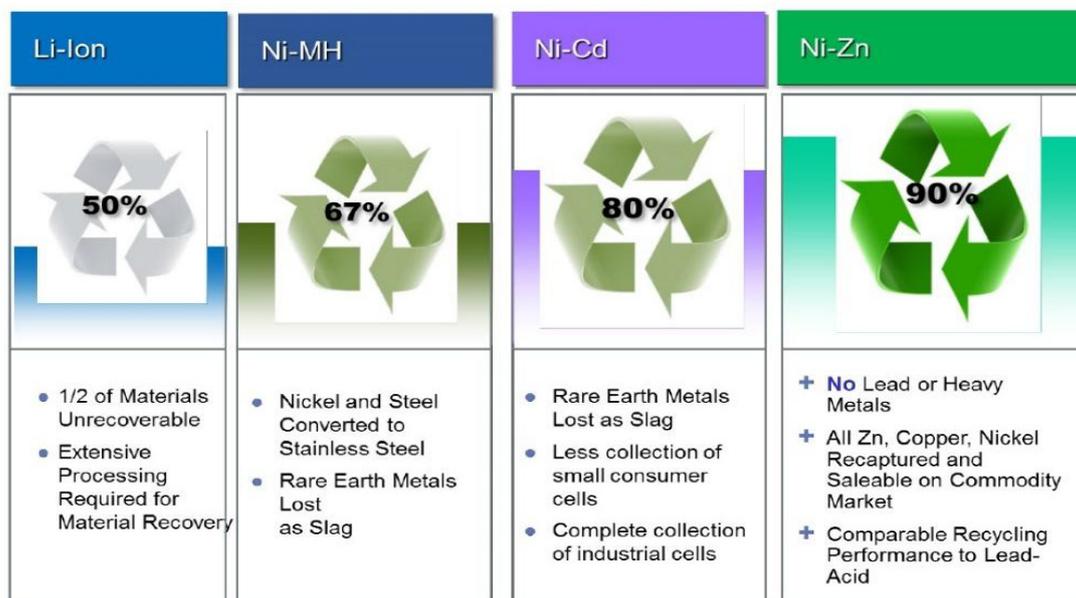
Fig. 1. Recyclability

However, some significant obstacles are still far away from a satisfactory level due mainly to the relative low power density and poor cycling stability of the Ni/Zn batteries due to the shape change, dendrite formation and corrosion of the zinc electrode leading to polarization, passivation and short-circuiting of full cell [8]. So far, many advanced techniques and strategies have been proposed to overcome the issues related to reducing the negative impact of zinc dendrites formation and their surface side reactions, which generally consist of coating the surface of the electrode. The

enhancement approach is mainly focused on structural optimization of the electrode, forming quasi-solid-state devices, applying some specific additives to the Zn electrode, optimization and modification of the electrolyte, use of double or triple layers separators, use of electrode substrate and current collectors increasing H_2 overvoltage, etc. [3, 4, 13-15].

The current collectors used for the two electrodes are playing an important role overcoming some of the existing shortcomings and thus optimizing the performance of the system. The three-dimensional (3D) substrates are the preferred solution and typically they are promoting prolonged life of the zinc electrode. It should be noted that the three-dimensional substrates significantly increase the internal electrochemically active area of the zinc electrodes, resulting in smaller current densities and achieving a longer life of the system.

A rechargeable nickel-zinc battery, based on enhanced and monolithic zinc sponge anodes has been developed showing a good energy density and cycle life [6, 16].

Copper is very widely used as a current-carrier due to its sufficiently good electrical conductivity. On the other hand, it has limited solubility in the alkaline electrolyte, which is enhancing the performance and lifetime of the batteries. Therefore, the use of copper substrate along with a galvanic coating of lead or tin are a favorable option, protecting the copper from dissolution and increasing the overvoltage of the zinc electrode to suppress the hydrogen evolution during overcharge, thus adversely improving the system performance [17].

In short, there is no one-size-fits-all solution; depending on the intended use of the battery, choices (in most cases a compromise) are made in the selection of the current collector.

Briefly recapping what was noted above, the problems associated with the zinc electrode can be summarized as shown below (in no order of importance):

1. Passivation (during discharge);

2. Shape change (during continuous charge/discharge);

3. Dendrite formation shortening the operational life (during charge/discharge);

4. H_2 evolution (during overcharging);

5. Solubility of zinc in the electrolyte (passage of zinc ions through the separator).

Having highlighted these major obstacles, the objective of the present work is to investigate and optimize the microstructure of the Zn electrode active mass by using different additives and wetting agents.

EXPERIMENTAL

1. *Zinc electrode* - The choice of the right binder and its used amount is very important during making of a good pasted Zn electrode. Most of the developed recipes indicated CMC (carboxymethyl cellulose) [18, 19] or HEC (hydroxyethyl cellulose) [20] as a good workable binder and indeed they are excellent binders, however being water soluble, over the time degrading into the electrolyte and the electrode integrity slowly goes down. In this study we are focusing on the use of a combination of CMC with an additional binder having increased stability in alkaline electrolyte. Polytetrafluoroethylene (PTFE) is a good choice, where the applied amount is critical – at higher amounts, the electrode resistance substantially increases, generating a lot of heat during charge and the output performance and life correspondingly goes down [21].

The basic recipe used is shown below:
1. 78 wt. % ZnO;
2. 10 wt. % metallic Zn powder;
3. 5 wt. % graphite flakes, mesh 325.99%;
4. 2 wt. % carboxymethyl cellulose (CMC);
5. 5 % PTFE (60 wt. % dispersion in H_2O).

The main component in the above shown recipe is ZnO. We used nanosized ZnO with particle size of 50 nm, offered by Ever Zinc. Pure 10 wt. % metallic Zn powder (Valerus) was also added to the active masses.

The experiments aiming to determine an optimal amount of PTFE, as well as of some surfactants, are summarized in Table 2.

Table 2. Zinc active mass variations

Binder	Surfactants			
	Without	Triton X-100	Dispex	Dispex + Triton X-100
2 wt. % CMC + 5 % PTFE	✓	✓	✓	✓
2 wt. % CMC + 8 % PTFE	✓	X	X	✓
5 - 12 % PTFE	✓	✓	✓	✓
2 wt. % CMC + 12 % PTFE	✓	X	X	✓

Fig. 2. Pasted Zn electrode

The Zn electrodes were prepared by applying the above-described paste compositions into Cu foam substrates with 45×65 mm dimensions, where the average active mass weight was 6-6.5 g as shown in Fig. 2.

2. *Nickel electrode* **-** As a Ni electrode during all of the experiments, we used commercial sintered Ni electrode with rated capacity of 115 mAhg^{-1} (Institute of Non-Ferrous Metals, Poznan, Poland) with dimensions of 85×40 mm as shown in Fig. 3.

Fig. 3. Sintered Ni electrode

3. *Electrolyte* **-** As an electrolyte alkaline solution of 30% KOH was used, in some of the experiments we applied gelling agents: PVA (135 000) + KOH; PVA (195 000) + KOH + TEAOH.

4. As a *Separator* "Viledon separator" with item number 700/18F was used.

5. *Electrochemical cell* - Exploiting the described electrodes, they were tested in a three-electrode configuration prismatic cell using a Hg/HgO reference electrode (Tianjin Aida Hengsheng Technology Development Co., Ltd.).

As marked above, the alkaline electrolyte in Ni/Zn cells did not directly participate in the electrochemical reaction, but it served only as a medium providing the corresponding ionic transport [25]. That's why typically these batteries were not required to be over flooded with electrolyte in order to reduce the solubility of the Zn electrode into the electrolyte. Most of the experiments were carried out in cells under semidry conditions. The cell assembly was equipped with a Hg/HgO reference electrode where the cell is limited in capacity by nickel electrode (negative/positive ratio >2), thus avoiding H$_2$ evolution, maintaining the Zn electrode to be always partially charged at the end of the charging step.

7. *Electrochemical tests* - In order to be properly activated, the assembled cell went through an initial formation cycle which is graphically shown in Fig. 4 below.

After properly activating the cell, a 2-step charge approach in order to avoid H$_2$ evolution as overcharge was applied. It first charges with constant current (CC) until a cell voltage of 1.9 V is reached, then continues charging, switching to constant voltage (CV) charging until the corresponding current drops to a predetermined level, usually C/40.

RESULTS AND DISCUSSION

Initially, experiments with different amounts of PTFE and surfactants were performed for 48 hours, (Fig. 5), then the cells were disassembled, electrodes were washed, dried and the weight loss was measured. It was found that the optimal amount of PTFE in the active mass should not exceed 5 wt. %. Use of larger amounts of PTFE significantly increased the electrode resistance, although smaller weight loss was measured. On the other side, using water soluble surfactants as ingredients leads to an increased electrode weight.

1. Run @ Room Temperature
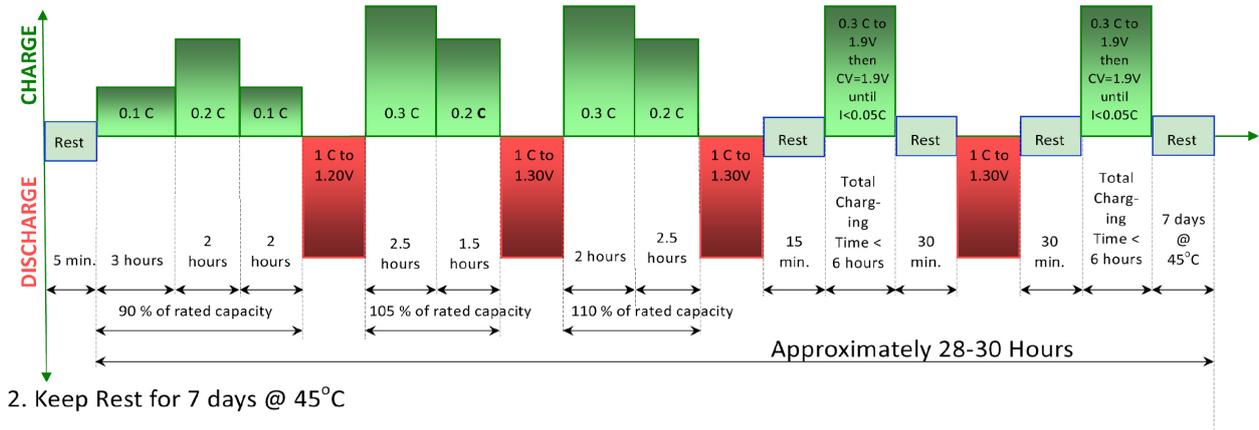
2. Keep Rest for 7 days @ 45°C

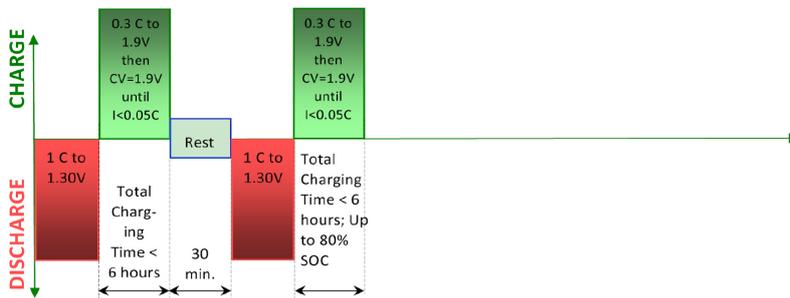3. Cool Down to Room Temperature and Determine the Capacity

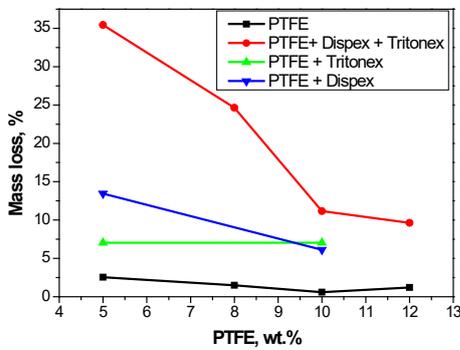**Fig. 4**. Initial formation cycles

Fig. 5. Electrode weight loss

The anticipated positive impact of using surfactants on cell discharge capacity was not found, as shown on Fig. 6, where cells using 5 wt. % PTFE with and without surfactants are compared.

Apparently, the use of surfactants increases the electrode weight loss, without providing measurable change in surface tension and better electrolyte penetration inside the electrode. For better understanding of such a relationship and comparison of resulting ohmic resistance, the following experiment was performed:
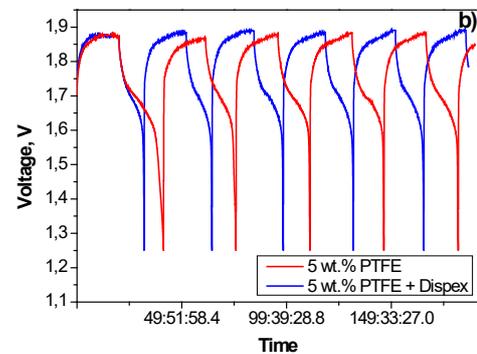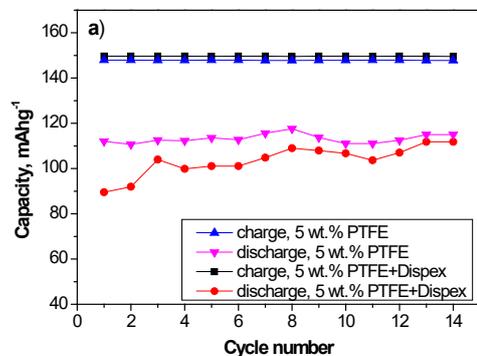

Fig. 6. Discharge capacity (a) and cell voltage profile for cells with and without Dispex surfactant (b)

At 50% DOD, short 30 sec. various current pulses were applied. Obtained voltage profiles were analyzed, where the first sharp voltage drop contributed to electrode ohmic resistance, while the second smooth drop represented the summary of all electrochemical overvoltage. The ohmic resistance for electrodes with and without surfactants was determined from the results obtained from 3 consecutive pulses at C/10, C/5 and C/2.

It seems that the use of surfactants reduces the electrode resistance to some degree, although such beneficial tendency was not clearly detected on our small-size electrodes. Probably, it will be better pronounced on larger-size electrodes and/or cells with more electrode pairs. However, as marked above, their use is increasing the electrode weight loss, and the potential beneficial effect will be forfeited with a short life expectancy.

Table 3 below summarizes the tested electrode compositions, while Figures 7 and 8 are showing the obtained discharge curves and, correspondingly, their efficiencies.

Table 3. Tested electrode compositions

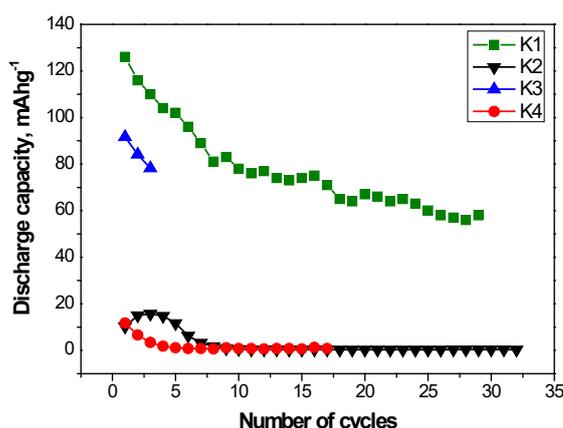| Paste Compositions			
Composition 1 (K1)	Composition 2 (K2)	Composition 3 (K3)	Composition 4 (K4)
78 wt. % ZnO nanosized	78 wt. % ZnO nanosized	73 wt. % ZnO nanosized	73 wt. % ZnO nanosized
10 wt. % Zn	10 wt. % Zn	10 wt. % Zn	10 wt. % Zn
5 wt. % graphite	5 wt. % graphite	5 wt. % graphite	5 wt. % graphite
5 % PTFE	5 % PTFE	8 % PTFE	10 % PTFE
2 wt. % CMC, dissolved in H_2O	2 wt. % CMC, dissolved in 5% KOH	2 wt.% CMC, dissolved in H_2O	2 wt. % CMC, dissolved in H_2O

Fig. 7. Discharge capacities for electrodes prepared with the compositions shown in the table above

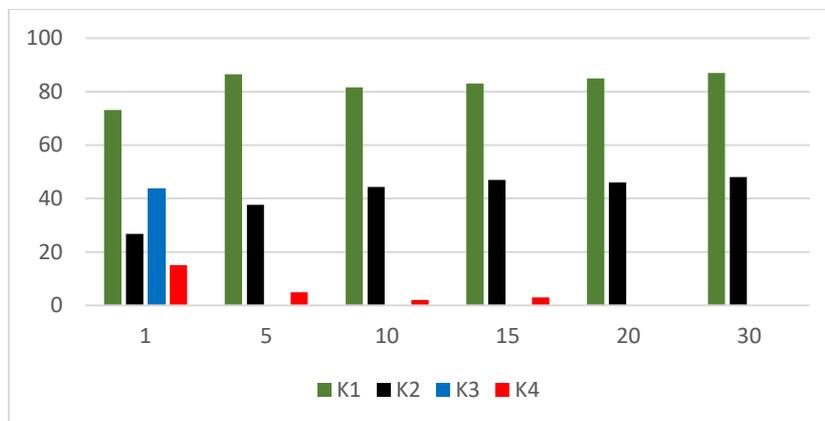**Fig. 8.** Current efficiencies at C/10 for K1, K2, K3 and K4 at different charge/discharge cycles: $(I_{discharge}/I_{charge}) \times 100$, %

It was found that the best behavior in respect to current efficiency is exhibited by the paste K1. The obtained result confirms the significant influence of the binder on the working characteristics of the zinc electrode.

The use of surfactants in some cases can lead to negative effects, so their careful selection is necessary.

CONCLUSIONS

It could be concluded that the use of surfactants is reducing the electrode resistance to some degree, although such beneficial tendency was not clearly detected on our small-size electrodes. Probably, it will be better pronounced on larger-size electrodes and/or cells with more electrode pairs. However, as marked above, their use is increasing the electrode weight loss, and the potential beneficial effect will be forfeited with a short life expectancy.

It is necessary to continue the work in this direction with the use of other binders and surfactants. The application of gelled or membrane electrolytes can also result in limiting the formation of Zn dendrites and a corresponding extension of the cell lifetime, which will be investigated in the second part of this work.

REFERENCES

1. K. M. Tan, T. S. Babu, V. K. Ramachandaramurthy, P. Kasinathan, S. G. Solanki, S. K. G. Raveendran, *J. Energy Storage,* **39**, 102591 (2021).
2. M. J. B. Kabeyi, O. A. Olanrewaju, *Front. Energy Res*., **9,** 743114 (2021).
3. T. K. A Hoang, L. Qin, T. Zhang, M. Zhou, J. Zhou, G. Fang, S. Liang, *Energy Stor. Mater.,* **34**, 545 (2021).
4. J. Zhou, L. Zhang, M. Peng, X. Zhou, Y. Cao, J. Liu, X. Shen, C. Yan, T. Qian, *Adv. Mater*., **34**, 2200131 (2022).
5. https://en.wikipedia.org/wiki/Comparison_of_comm ercial_battery_types.
6. L. Panpan, J. Zhaoyu, X. Jin, *Energy Stor. Mater.,* **12**, 232 (2018).
7. Y. Shang, D. Kund, *Batteries Supercaps.,* **5**, e202100394 (2022).
8. R. E. F. Einerhand, W. Visscher, *J. Electrochem. Soc.*, **138**, 7 (1991).
9. F. R. McLarnon, E. J. Cairns, *J. Electrochem. Soc*., **138**, 645 (1991)
10. Y. Zeng, Y. Meng, Z. Lai, X. Zhang, M. Yu, P. Fang, M. Wu, Y. Tong, X. Lu, *Adv. Mater.,* **44**, 29 (2017).
11. D. Squiller, R. Brody, *NSNTI Nanotech.,* **1**, 690 (2011).
12. M. Gong, Y. Li, H. Zhang, B. Zhang, W. Zhou, J. Feng, H. Wang, Y. Liang, Z. Fan, J. Liub, H. Dai, *Energy Environ. Sci.,* **7**, 2025 (2014).
13. Y. Liu, Y. Liu, Y, X. Wu, *Chem. Rec*., **22**, e202200088 (2022).
14. K. Zhao, F. Liu, G. Fan, J. Liu, M. Yu, Z. Yan, N. Zhang, F. Cheng, *ACS Appl. Mater. Interfaces,* **13**, 47650 (2021).
15. J. Liu, C. Guan, C. Zhou, Z. Fan, Q. Ke, G. Zhang, C. Liu, J. Wang, *Adv. Mater*., **28**, 8732 (2016).
16. F. Parker, C. N. Chervin, I. R. Pala, M. Mahler, M. F. Quick, J. Long, D. R. Rolison, *Science,* **356**, 415 (2017).
17. H.Wang T. R. Watkins, S. Simunovic, J. A. Turner, *ACS Nano,* **16**, 17139 (2022).
18. J. Li, N. Zhuang, J. Xie, Y. Zhu, H. Lai, W. Qin, *ACS Appl. Mater. Interfaces*, **11**, 15581 (2019).
19. Y. Li, Q. (Ray) Zeng, I. R. Gentle, D.-W. Wang, *J. Mater. Chem., A*, **5**, 5460 (2017).
20. M. A. Ramlli1, Yu K. X. Yu, Y. W. Siew, M. I. N. Isa, *ASM Sci. J., Special Issue* **1**, 47 (2018).
21. Y. Nishi, S. Iizuka1, M. C. Faudree, R. Oyama, *Mater. Trans*., **53**, 940 (2012).
22. C. Zhai, D. Zhao, Y. He, H. Huang, B. Chen, X. Wang, Z. Guo, *Batteries, 8,* 153, (2022).