**Development of Intermediate Temperature Sodium Nickel Chloride Rechargeable
Batteries using Conventional Polymer Sealing Technologies**

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Abstract

Developing advanced and reliable electrical energy storage systems is critical to fulfill global energy demands and stimulate the growth of renewable energy resources. Sodium metal halide batteries have been under serious consideration as a low cost alternative energy storage device for stationary energy storage systems. Yet, there are number of challenges to overcome for successful market penetration, such as high operating temperature and hermetic sealing of batteries that trigger an expensive manufacturing process. Here we demonstrate simple, economical, and practical sealing technologies for Na-NiCl₂ batteries operated at an intermediate temperature of 190°C. Conventional polymers are implemented in planar Na-NiCl₂ batteries after a prescreening test, and their excellent compatibilities and durability are demonstrated by a stable performance of Na-NiCl₂ battery for more than 300 cycles. The sealing methods developed in this work will be highly beneficial and feasible for prolonging long battery cycle life and reducing manufacturing cost for Na-based batteries at elevated temperatures (<200°C).

Keywords: Na-metal halide batteries, Na-MH battery, Zebra, Intermediate temperature, Polymer sealing, Stationary Energy Storage.

Introduction

Na-based batteries have gained recognition for next-generation stationary energy storage systems due to highly abundant and low cost Na resources and suitable reduction potential (-2.7 V vs. a standard hydrogen electrode).[1-5] Among all Na-based batteries under development, Na-metal halide (Na-MH) batteries, in which the cathode materials are composed of transition metal halides such as NiCl_2 , FeCl_2 , or mixed Ni-FeCl_2 , have become one of the best candidates to satisfy the increasing energy demand for a wide range of energy storage applications.[6-10]

The essential parts of Na-MH systems are a molten sodium anode, a β'' -alumina solid-state electrolyte (BASE), a secondary electrolyte, and a metal-halide cathode. A Na-MH battery can be assembled in a fully discharged state, using sodium chloride (NaCl) and metal powders without handling extremely pyrophoric metallic sodium and hygroscopic metal halides. The BASE, a sodium-ion-conducting ceramic, prevents crossover and battery self-discharge (100% coulombic efficiency) for a broad range of operational conditions. Furthermore, the use of an inorganic secondary electrolyte, sodium aluminum tetrachloride (NaAlCl_4), provides high Na^+ ion conductivity and superior safety (low fire hazard level).[7, 11-14] Despite these attractive features, Na-MH batteries have not successfully achieved further market penetration because of challenges including complicated cell architecture, high operating temperature, and degradation of battery performance over cycles.[15-19]

Typically, a conventional tubular type Na-MH battery is operated at high temperatures above 280°C to obtain acceptable electrochemical performances. Our recent work on a planar type Na-MH battery demonstrated that remarkable electrochemical

performances can be achieved even at an intermediate temperature (IT) of 190°C.[20-22] The overall electrochemical performance of the IT Na-MH battery exhibits a stable cycle life of over 1000 cycles with an excellent capacity retention. The high energy density and superior cycle stability are attributed to the slower particle growth of cathode materials (NaCl and Ni) at 190°C compared to that at 280°C.[21] Moreover, lowering the operating temperature of a Na-MH battery from 280°C to 190°C opens great opportunities to adopt cost-effective sealing technologies for the cell architecture. For instance, high operating temperature requires complicated and high cost sealing methods (such as glass seals, thermal compression bonding, and electron beam welding), which are critical for high temperature operating Na-MH batteries to achieve airtight and corrosion-free seals against a molten sodium anode and a halide-based secondary electrolyte. In contrast, the lower operating temperature of 190°C could allow conventional polymers to be used as sealing materials in Na-MH batteries.

Figure 1. Schematic structure and composition of polymer candidates as sealing materials.

In this study, we have evaluated and optimized various conventional polymer materials, which are listed in Fig. 1, as candidates for sealing materials in planar design Na-NiCl₂ batteries. A prescreening test was performed to quickly select sealing materials from among those high temperature polymers for the cathode and the anode for the battery operating temperature of 190°C. The selected polymers have been implemented in Na-NiCl₂ cells, and their compatibility was investigated by monitoring the electrochemical performance with cycling. The polymer-sealed cell could be cycled more than 300 cycles with stable cell performance. Use of the conventional polymers demonstrated in this work can be a cost-effective, reliable, and practical solution for Na-

MH battery technologies, and provides a great opportunity for developing low cost planar sodium battery technologies.

Experimental

Polymer prescreening tests

Prescreening tests were performed in a glove box on eight different types of polymer films: ultra-high-molecular-weight polyethylene (UHMW-PE), polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), perfluoroalkoxy alkane (PFA), polyether ether ketone (PEEK), polyimide (Kapton), and ultra-temperature polyetherimide (Ultem PEI), which were purchased from McMaster-Carr. Na ($T_m = 97.72\text{ }^{\circ}\text{C}$) and NaAlCl_4 (secondary electrolyte, $T_m = 157\text{ }^{\circ}\text{C}$) in glass vials were placed on a 200°C hot plate and the polymers were soaked in the molten Na and NaAlCl_4 for 5 mins. PTFE, FEP, and PFA are immersed in NaAlCl_4 for 72 hours for testing the long time stability. The polymers retrieved from molten Na and NaAlCl_4 are shown in Fig. S1. The melting temperatures (T_m) of various polymers were also measured after cleaning by isopropanol to remove possible contaminants by differential scanning calorimetry (DSC) analysis, which was conducted in the air on a NETZSCH-STA-449C thermal analyzer over the temperature range $25\text{--}500^{\circ}\text{C}$ with a heating rate of $10^{\circ}\text{C}/\text{min}$ to study their thermal properties. The results are shown in the Supplementary Information (Fig. S2).

Sample preparation and battery assembly

Electrochemical cells were prepared in a planar format consisting of a Ni/NaCl granule cathode (157 mAh , $52.3\text{ mAh}/\text{cm}^2$), NaAlCl_4 secondary electrolyte, and a homemade β'' -alumina / yttria-stabilized zirconia (YSZ) composite solid-state electrolyte (BASE). In the following, we briefly explain essential parts of the preparation procedures; more detailed information can be found in previous publications.[21, 22]

Cathode powders consist of Ni powder (Novamet, Type 225, particle size in 1-2 μm), NaCl powder (Alfa Aesar, 99.9%,), and additives (>99%, Al powder, NaI, NaF and FeS, Sigma Aldrich). **Ni/NaCl Cathodes were prepared by low-energy ball milling powders at 50 rpm for 24 hours (the ratio of mass/balls = 0.6), and then granulated at 9 MPa compact pressure using a granulator (Freund TF-LABO).** Sodium tetrachloroaluminate (NaAlCl_4) was prepared through high temperature synthesis by mixing NaCl and AlCl_3 . An excess of NaCl was used to avoid the formation of Lewis-acidic melts. BASE discs were fabricated with a diameter of 3 cm and a thickness of 500 μm using the vapor-phase conversion method.[13, 23] All the polymer candidates after the prescreening test were cut into a ring shape for sealing experiments.

Figure 2. Schematic view of a planar Na- NiCl_2 cell. Exploded view (a) and cross-section view (b) of the cell.

Fig. 2 displays a simple planar cell configuration, which consists of end caps (stainless steel), α -alumina (99.5% purity) fixture, and polymer rings. A BASE disc was first glass-sealed to an α -alumina fixture and a helium leak test was carried out to verify no leakage from the BASE and the glass-sealed fixture. The anode side of the BASE surface was heat treated at 400°C to improve sodium wetting after applying **a saturated lead acetate (>99%, Sigma Aldrich) aqueous solution**. Cathode granules (1.0 g) and

NaAlCl₄ (0.8 g) were loaded onto the cathode side of the fixture at an elevated temperature of 200°C and then vacuum infiltrated. To facilitate an initial contact between BASE and the anode side, a small amount of metallic sodium was added to the anode shim. The polymer rings were placed on the top and the bottom of the fixture (Fig. 2a) as a primary sealing. The cell was enclosed with the end caps and screwed shut to fix all the parts together. All cell assembly process were conducted in a nitrogen-purged glove box (O₂ and H₂O < 0.1 ppm). For the test using UHMW-PE, a secondary sealant was applied to the edges of the fixture directly contacting the end caps along with the polymers, as shown in Fig. 2b.

Electrochemical tests

The experiments were set for three different purposes: polymer compatibility for anode sealing (Exp.1), polymer compatibility for cathode sealing (Exp.2), and effect of secondary sealants for long-term applications (Exp.3). In Exp. 1, cells were sealed with a combination of UHMW-PE (anode)|FEP (cathode) and PVDF|FEP, respectively. In Exp. 2, cells were sealed with PVDF|gold, PVDF|FEP, PVDF|PFA, and PVDF|PTFE. In Exp. 3, cells were sealed with UHMW-PE for both cathode and anode, and silicon-based (Aremco, CP4040) and epoxy-based sealants (Duralco, 4703) were applied as a secondary sealants, respectively.

Initially, all cells were cycled at 190°C between the cutoff voltages of 2.8 V (charge limit) and 1.8 V (discharge limit) at a constant current of 10 mA for conditioning cycles. After the initial conditioning cycles, fixed-capacity cycling tests were conducted at a charge current of 20 mA and a discharge current of 30 mA (C/3). The capacity

window for the cycling tests is between 22% (35 mAh) and 80% (125 mAh) of the state of charge (SOC) window (90 mAh, 57% of theoretical capacity).

Scanning electron microscopy (SEM)

In order to detect the changes in particle size of the cathode materials, SEM studies were performed. For the cross-sectional images of the fracture surface, the cathodes were carefully collected after disassembling the battery cells in the glove box and quickly transferred to the SEM chamber to minimize the time of exposing to the air. A JEOL JSM-7001F field emission SEM with silicon drift detector were used. An Oxford energy dispersive x-ray spectroscopy (EDX) analysis was conducted to identify Na and Ni element maps.

Results and Discussion

Table 1. Prescreening results of polymer candidates

#	Polymer	IUPAC name	Chemical formula	T _m *	Measured T _m	NaAlCl ₄	Na
1	UMHW-PE	Ultra-high-molecular-weight Polyethylene	(C ₂ H ₄) _n	130–136 °C	125.7 °C	Good	Good
2	PVDF	Polyvinylidene fluoride	(C ₂ H ₂ F ₂) _n	177 °C	164.7 °C	Fail	Good
3	PTFE	Polytetrafluoroethylene	(C ₂ F ₄) _n	326.8 °C	342.3 °C	Good	Fail
4	FEP	Fluorinated ethylene propylene	(C ₂ F ₄) _n -(C ₂ F ₃ CF ₃) _m	260 °C	281.3 °C	Good	Fail
5	PFA	Perfluoroalkoxy alkane	(C ₂ F ₄) _n -(C ₂ F ₃ OR') _m	315 °C	290.9 °C	Good	Fail
6	PEEK	Polyether ether ketone	(C ₁₉ H ₁₂ O ₃) _n	343 °C	349.1 °C	Fail	Fail
7	Kapton Polyimide	Polyimide	(C ₂₂ H ₁₀ N ₂ O ₅) _n	—	—	Fail	Fail
8	Utem (PEI)	Amorphous thermoplastic polyetherimide	(C ₃₇ H ₂₄ O ₆ N ₂) _n	204-232 °C	204-230 °C	Fail	Fail

* T_m values from a reference resource (Wikipedia)

Table 1 shows results of prescreening tests of the polymers' stability toward NaAlCl₄ and Na. Besides the primary purpose of using polymers as a sealing method, when selecting materials for the battery operation it is important to consider possible polymer decomposition by secondary electrolytes such as NaAlCl₄ in cathodes and molten sodium anodes, as well as their melting temperatures. Four of the polymers (PTFE, FEP, PFA, and UHMW-PE) were nonreactive with NaAlCl₄ melt, suggesting suitable sealing candidates for cathodes, while only two of them (PVDF, UHMW-PE) were stable with molten sodium anodes at 200°C. The rest of the polymers underwent color changes due to chemical reactions with Na or NaAlCl₄ as shown in Fig. S1. It is a note of that white residual remains (Fig. S1) on the polymer films in the prescreening test are NaAlCl₄ melts (T_m=157 °C) at room temperature. DSC analysis (Fig. S2) showed that the melting point temperatures of all polymers. The measured T_m values are slight different from the reference data and we believe the error (±10%) is associated with additives in commercial polymers, systematic error from DSC, and precision of T_m

determination. Despite this, the overall results correlate well with the melting temperatures reported in the literature.

Figure 3. Electrochemical performance of the cells using PVDF (a, b) and UHMW-PE (c, d) polymer for the anode at 190°C. (a) Voltage profiles for the cell with PVDF collected at the initial charge/discharge cycle (broken line) and at 1st (black), 50th (red), 100th (blue) cycles from the fixed-capacity tests. The yellow box represents the SOC operating window. Four distinct voltages at the beginning of charge (BOC)/ discharge (BOD) and at the end of charge (EOC)/ discharge (EOD) were used to analyze the effects of the sealing technologies on cell performance. (b) Plot of EOC and EOD voltages for the cell with PVDF. (c) Voltage profiles for the cell with UHMW-PE collected at 1st (black), 50th (red), and 100th (blue) cycles in the fixed-capacity tests. (d) Plot of EOC and EOD voltages for the cell with UHMW-PE.

To evaluate the effectiveness of the polymers when used at the anode as an air leak prevention material, PVDF and UHMW-PE were applied to the anode side of the cell fixture. (FEP was tentatively used to seal the cathode side for both cells, as the

cathode compositions are relatively less air-sensitive.) The assembled cells were cycled in a fixed-capacity window between 22% and 80% SOC to demonstrate their compatibilities for the Na-NiCl₂ system operating at 190°C (Exp.1). The electrochemical behaviors of the cell sealed with UHMW-PE and PVDF at the anode at 190°C are shown in Fig. 3. The cell voltage curve (solid line, Fig. 3a) for a complete cycle has four distinct voltage points at the beginning of charge (BOC) and discharge (BOD) and at the end of charge (EOC) and discharge (EOD). In this study, the difference between BOC and BOD voltages was used to measure overall overpotential and the internal resistance of a cell, particularly for the BASE and electrolytes. For instance, the voltage profile (dotted line) for the cell with PVDF collected during the initial charge/discharge cycle at a constant current of 10 mA shows smaller overpotential than the profiles (solid line) collected during fixed-capacity cycling at 20 mA for charge and 30 mA for discharge due to the lower current. Generally, the voltages at EOC and EOD reflect the corresponding SOC during the fixed-capacity cycling, and thus more sensitive to the status of cells. When a cell approaches failure due to leakage occurring on either the cathode or anode side, an increase in EOC voltage to 2.8 V (charge limit) or decrease in EOD voltage to 1.8 V (discharge limit) should be observed, respectively. In addition, a shift of SOC operating window will be detected when there are limitations of charge or discharge capacities caused by degradation/evaporation of cathode materials or oxidation of the anode. Therefore, analysis of EOC and EOD were mainly performed to evaluate the polymer sealing effectiveness and existence of air leakage.

The voltage curves of the cell sealed with PVDF at the 1st, 50th, and 100th cycle were well overlapped as the cycle number increased (Fig. 3a). The absence of shift in the

cycling window is clear evidence of no capacity degradation. Moreover, Fig. 3b shows that the cell voltages at around 2.7 V (EOC) and 2.2 V (EOD) were fairly stable throughout the cycles, suggesting that the cell has been effectively protected from the air leakage. A gradual increase in EOD voltage (improvement of the cell performance) was observed, and it is attributed to improvement of wettability of molten Na on the BASE as well as effective protection of the anode from air by the use of the polymer sealing technique. Generally, PVDF exhibits better mechanical properties than those of fully fluorinated polymers because of the shielding effect of the F atoms in CF_2 adjacent to CH_2 groups. Despite its relatively lower melting point compared to fully fluorinated polymers, it exhibits the highest flexural strength, relatively very low deformation rates under pressure, and high heat resistance.[24, 25] Also, PVDF is highly resistant to most inorganic/organic acids, bases, hydrocarbons, and oxidizing agents. We assume that these aspects could play a significant role when PVDF is used as an adhesive in physically bonding the cell fixture to the cell end cap and effectively protecting the anode from air without any side reactions with molten Na.

The cell with UHMW-PE also shows no significant shift in SOC window with reasonable electrochemical performance over 100 cycles, as shown in Fig. 3c. However, continuous fluctuation with a slight decrease in EOD was observed, indicating that a gradual discharge capacity problem was occurring on the anode side (Fig. 3d). The decrease in EOD can be associated with either a poor wetting of molten Na or insufficient Na transfer due to the oxidation of anodes. The former situation usually is mitigated after the initial charge/discharge cycles because the repeating Na transfer at a low current improves the molten Na distribution on the BASE surface while the latter leads to

continuously descending and unsteady voltage profiles, suggesting that the major cause of degradation with UHMW-PE is the stability of the anode seal. The properties of UHMW-PE are basically very similar to PVDF, since PVDF is fluorinated forms of PE ($-(\text{CH}_2-\text{CH}_2)_n-$). [26] However, UHMW-PE has a lower melting point and higher oxygen permeability than conventional fluorinated polymers including PVDF. Also, the thermal decomposition temperature of UHMW-PE and its chemical and mechanical properties can be weakened in an extreme environment since the general characterization of polymers is performed under atmospheric conditions. [24] Therefore, we suggest the relatively low melting point of UHMW-PE may cause gradual thermal degradation as well as oxygen penetration under the continuous high-temperature condition, which allow the gradual anode oxidation. More precise measurement of the changes in polymer properties would be required to test our hypothesis. Although the cell voltage profile with UHMW-PE, particularly EOD, was not as stable as that for the cell with PVDF, the overall results suggest that UHMW-PE can be a good sealing material for short-term applications or lab-scale experimental purposes.

Figure 4. EOC voltage profiles of Na-NiCl₂ cells using different types of polymers as a sealing material for 100 cycles. The cathode sides of the cells were sealed with (a) gold (black), (b) FEP (red), (c) PFA (blue), and (d) PTFE (green). PVDF was used to seal the anode sides. The cell sealed with PVDF/gold was tested as a reference cell since gold is chemically and thermally stable toward the cathode side. Stable EOC demonstrates a great effectiveness of the conventional polymers as sealing materials for Na-NiCl₂ batteries. See text for more detailed discussion.

On the cathode side, the prescreening tests confirmed that FEP, PFA, and PTFE are chemically stable to secondary electrolyte at 200°C, and these polymers were applied to evaluate their compatibilities as a cathode sealing material (Exp. 2). The anode side of the cells was sealed with a **PVDF ring**, since its suitability on the anode side was verified. The cell using a gold metal O-ring on the cathode side (with PVDF on the anode side) was tested as a reference cell since gold has strong chemical inertness toward cathode materials and good durability in air at a high temperature. **Fig. 4 illustrates the voltages at EOC for the cells using gold, FEP, PFA, and PTFE. The change of EOC over 100 cycle (ΔV_{EOC}) was used to qualitatively compare the cell performance. As expected, the reference cell shows a stable EOC voltage over 100 cycles with $\Delta V_{\text{EOC}} = -13.8$ mV, which is indicating an improvement of the cell performance, which most likely due to the improved Na wettability on the anode (Fig. 4a). The use of FEP provides an excellent EOC voltage stability with $\Delta V_{\text{EOC}} = 0.3$ mV. In contrast to the cells using gold and FEP for cathodes, the other two cells with PFA (Fig. 4c) and PTFE (Fig. 4d) show slightly higher ΔV_{EOC} of 60.3 mV and 30.0 mV, respectively. A positive ΔV_{EOC} indicates that the over-potential of the charge process, which is the oxidation of Ni cathode, is increased most likely due to the evaporation of melts. To confirm the major cause of the increase in EOC and the effectiveness of the polymer sealing, we added extra melt and resealed the cell with a fresh PFA film ring after disassembling the cathode side of the cell in the glove box. As we expected, the EOC voltage moved from 2.7 V to a lower value, around 2.65 V, and stabilized for the subsequent cycles (Fig. S4). This again clearly demonstrated that PFA is relatively less stable in completely protecting the cathode side and gradually allows melt evaporation during cycling. Although all three fluorinated**

polymers have very similar chemical and general properties, such as melting point, thermal expansion, and thermal conductivity, FEP has remarkably lower absorption of water (<0.1%) compared to PFA and PTFE (<0.3%).[24, 26] This suggests that the most effective reduction of cathode degradation and melt evaporation, which are in good agreement with cell tests shown above, can be achieved by the use of FEP. The other two polymers can be used as alternatives since the cell degradation rates are practically still low. **Indeed, a Na-NiCl₂ cell assembled with PVDF/FEP sealing shows a remarkable cell stability over 300 cycles as shown in Fig. S3.**

Figure 5. SEM images of cathode materials from the cell sealed with PVDF for anode and FEP for cathode. (a,c) The surface images of the cathode after fully discharging. (b,d) Ni and Na mapping images of (a) and (c), respectively. The yellow circles shown in the SEM image of (c) indicate NaCl particles in Na mapping image of (d).

It has been understood that the degradation of Na-NiCl₂ is closely associated with growth of cathode particles such as Ni and NaCl.[18, 21] The particle growth will reduce the active area of Ni and retard the dissolution of NaCl, which will lead to the higher over-potential and the capacity degradation. The SEM/EDX analysis of the cell sealed with PVDF and FEP after 100 cycles is displayed in Fig. 5. The EDX mapping confirms that the brighter areas represent Ni particles (Fig. 5b) while the bright red areas are NaCl crystals (Fig. 5d). The initial particle sizes of Ni and NaCl powders shown in Fig. S5 were typically ~2 μm and 30-50 μm , respectively. Fig. 5a and 5c clearly show that there is no significant growth in cathode particles after 100 cycles, and it is in good agreement with the stable EOC profiles observed in Fig. 4b.

Our data has shown that UHMW-PE could be a good selection for sealing materials as it shows good chemical stability with both cathode and anode compositions. However, the gradual discharge problem in Fig. 3d results implies that its ability to seal anodes might not be sufficient for long-term purposes. Hence, we extended the scope of our sealing technologies for a long-term cell test by adding secondary sealants over the primary polymer seal as shown in Fig. 2b. The cells sealed with UHMW-PE for both cathode and anode were tested to monitor the effect of a secondary sealant (Exp. 3). Different types of sealants, namely silicon-based (Aremco CP4040) and epoxy-based (Duralco 4703) adhesives, were examined. Fig. 6 displays the voltage plots of the cells with application of a silicon-based secondary seal. The plot shows that the cell sealed with a secondary seal (silicon-based adhesive) over the UHMW-PE shows excellent cycling stability over 300 cycles in contrast the cell only having UHMW-PE (Fig. 3d). The EOD voltage plot also exhibits a stable performance while the EOC voltages show a

slight increase during 300 cycles. Furthermore, the cell using the epoxy-based secondary sealant shown in Fig. S6 also exhibits extension of cycle life with fairly stable voltage profiles for more than 250 cycles. It is a note of that we have observed that using the secondary sealant alone as a primary sealant have typically shown either a rapid degradation or an immediate cell failure due to reactions between secondary sealant materials (i.e. silicon) and melts/sodium.

Figure 6. Voltage plot of the cell primary sealed with UHMW-PE and secondarily sealed with the silicon-based adhesive (CP4040). The voltages at the end of charge (EOC, black) and discharge (EOD, red) were collected during cycling.

Our observation suggests that the role of the secondary sealant can be significant over the primary sealant. We believe that the degradation of UHMW-PE is accelerated by

moisture and oxygen at the cell operating temperature. Applying secondary sealant will greatly reduce the exposure of UHMW-PE to moisture and oxygen, therefore, double-sealing technologies can maximize a stable cell performance and insure a long cell cycling life.

An important goal of our study is to develop low cost, durable, and simple sealing methods for Na-MH battery systems. The conventional polymers selectively chosen for each electrode show that they can prevent air leakage for more than 100 cycles. Without secondary sealant, PVDF and FEP are the simplest and a reasonable combination for long-term cycling. Application of additional sealant can not only improve a good electrochemical performance, but also extend battery cycle life. Moreover, it can be feasible for scaled-up battery applications.

Conclusions

Design of planar Na-MH batteries has been challenging for long-term and large-scale batteries because of poor sealing methods. Our study provides an effective, economical, and feasible solution to hermetic sealing problems. Due to high operating temperature, possible corrosion from molten sodium, and cathode composition, conventional polymers had not been considered as suitable sealing materials for conventional tubular Na-NiCl₂ batteries. In this work, we demonstrate the successful implementation of the selected polymers as sealants at the intermediate temperature of 190°C. Effective prevention of air leakage was successfully achieved in whole cells using various polymers for at least 100 cycles, and the cell primarily sealed with a combination of PVDF and FEP achieved the most stable electrochemical performance (>300 cycles). Moreover, the use of additional sealants significantly improve the long term stability for the cells primarily sealed with UHMW-PE. We believe that both conventional polymers and additional sealants tested in this work can be applied to Na-MH batteries. More importantly, this simple and economical sealing method can provide an alternative approach for Na-based batteries (i.e., Na-S, other types of Na-MH batteries) that require high operating temperature for long cycle life.

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References

- [1] J.L. Sudworth, A.R. Tilley, *The Sodium Sulfur Battery*, Kluwer, New York, 1985.
- [2] M.D. Slater, D. Kim, E. Lee, C.S. Johnson, *Adv. Funct. Mater.*, 23 (2013) 947-958.
- [3] B. Dunn, H. Kamath, J.M. Tarascon, *Science*, 334 (2011) 928-935.
- [4] X.C. Lu, G.S. Li, J.Y. Kim, J.P. Lemmon, V.L. Sprenkle, Z.G. Yang, *Energy Environ. Sci.*, 6 (2013) 1837-1843.
- [5] K. Jung, S. Lee, Y.-C. Park, C.-S. Kim, *J. Power Sources*, 250 (2014) 1-14.
- [6] G.S. Li, X.C. Lu, J.Y. Kim, V.V. Viswanathan, K.D. Meinhardt, M.H. Engelhard, V.L. Sprenkle, *Adv. Energy Mater.*, 5 (2015).
- [7] J.L. Sudworth, *J. Power Sources*, 51 (1994) 105-114.
- [8] R.J. Bones, D.A. Teagle, S.D. Brooker, F.L. Cullen, *J. Electrochem. Soc.*, 136 (1989) 1274-1277.
- [9] P.T. Moseley, R.J. Bones, D.A. Teagle, B.A. Bellamy, R.W.M. Hawes, *J. Electrochem. Soc.*, 136 (1989) 1361-1368.
- [10] R.C. Galloway, S. Haslam, *J. Power Sources*, 80 (1999) 164-170.
- [11] C.H. Dustmann, *J. Power Sources*, 127 (2004) 85-92.
- [12] J.L. Sudworth, *J. Power Sources*, 100 (2001) 149-163.
- [13] X.C. Lu, J.P. Lemmon, V. Sprenkle, Z.G. Yang, *JOM*, 62 (2010) 31-36.
- [14] S. Ha, J.K. Kim, A. Choi, Y. Kim, K.T. Lee, *Chemphyschem*, 15 (2014) 1971-1982.
- [15] X.C. Lu, G.G. Xia, J.P. Lemmon, Z.G. Yang, *J. Power Sources*, 195 (2010) 2431-2442.
- [16] K.B. Hueso, M. Armand, T. Rojo, *Energy Environ. Sci.*, 6 (2013) 734-749.

- [17] H. Kim, D.A. Boysen, J.M. Newhouse, B.L. Spatocco, B. Chung, P.J. Burke, D.J. Bradwell, K. Jiang, A.A. Tomaszowska, K.L. Wang, W.F. Wei, L.A. Ortiz, S.A. Barriga, S.M. Poizeau, D.R. Sadoway, *Chem. Rev.*, 113 (2013) 2075-2099.
- [18] G.S. Li, X.C. Lu, J.Y. Kim, J.P. Lemmon, V.L. Sprenkle, *J. Mater. Chem. A*, 1 (2013) 14935-14942.
- [19] E. Gerovasili, J.F. May, D.U. Sauer, *J. Power Sources*, 251 (2014) 137-144.
- [20] X.C. Lu, G.S. Li, J.Y. Kim, D.H. Mei, J.P. Lemmon, V.L. Sprenkle, J. Liu, *Nat. Commun.*, 5 (2014).
- [21] G.S. Li, X.C. Lu, J.Y. Kim, K.D. Meinhardt, H.J. Chang, N.L. Canfield, V.L. Sprenkle, *Nat. Commun.*, 7 (2016) 10683.
- [22] G.S. Li, X.C. Lu, C.A. Coyle, J.Y. Kim, J.P. Lemmon, V.L. Sprenkle, Z.G. Yang, *J. Power Sources*, 220 (2012) 193-198.
- [23] A.V. Virkar, J.-F. Jue, K.-Z. Fung, U.S. Pat. 6,117,807, 1998.
- [24] J.G. Drobny, *Technology of fluoropolymers*, Boca Raton, FL, CRC Press LLC, 2001.
- [25] M. Kutz, *Applied plastics engineering handbook: processing and materials*, Elsevier Science, Oxford, UK, 2011.
- [26] H.F. Mark, *Encyclopedia of polymer science and technology*, concise 3rd ed., John Wiley & Sons Inc, Hoboken, New Jersey, 2007.