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Source Journal of Power Sources, v. 416, March 2019, p. 21-28

Version Accepted Version

DOI 10.1016/j.jpowsour.2019.01.082

Publisher Elsevier

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**Stabilizing Mn-containing Cathode and Na-metal Anode with a
Na₃Zr₂Si₂PO₁₂/PVDF-based Solid-State Electrolyte**

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ABSTRACT

The dissolution of Mn ions from Mn-containing cathodes and the growth of Na dendrites are two critical issues that deteriorate the life time of Na batteries. In this work, we developed a novel solid-state composite-polymer-electrolyte (CPE) based on a polyvinylidene fluoride (PVDF) matrix and $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NZSP) fillers, PVDF/NZSP-CPE, to simultaneously tackle these two problems. Elemental and morphology analysis show that the PVDF/NZSP-CPE effectively impedes the dissolution and migration of Mn ions from the $\text{Na}_{0.67}\text{MnO}_2$ (NMO) cathode as well as facilitates the uniform deposition of Na on the anode. A facile interface modification is applied to improve the contact between the PVDF/NZSP-CPE and electrodes, which reduces the interfacial resistances and greatly delays the growth of Na dendrites. Consequently, the NMO/Na cell with the PVDF/NZSP-CPE displays a significant improvement in cyclic stability and rate performance, without sacrificing the specific capacity, compared to that of a cell using an organic-liquid electrolyte. Therefore, this work provides an effective way to improve the cycle life of Na batteries by stabilizing both electrodes with a CPE and can be readily applied to other batteries, e.g. Li batteries.

1. Introduction

Rechargeable Na-ion batteries (NIBs) have long been considered as promising alternatives to Li-ion batteries (LIBs) especially for grid-scale electrical energy storage applications because, relative to Li, Na is cheaper, more abundant, and more uniformly distributed around the world¹⁻⁴. Owing to the similarities between LIBs and NIBs, NIB equivalents of LIB cathode materials, including oxides and phosphates, have been extensively studied^{2,4}. Among those, Mn-containing oxides, Na_xMnO_2 ($x \leq 1$), have attracted substantial interest because of their sizeable reversible capacity⁴⁻⁸ as well as Mn's abundance and cost-effectiveness compared to Co and Ni^{1,5-7,9,10}. However, these Na_xMnO_2 cathodes suffer from poor capacity retention because of their structural instability. Generally, the migration of Mn ions into Na layers^{5,11} and oxygen layer gliding^{5,8} significantly affect the stability of Na_xMnO_2 . Trivalent Mn^{3+} is also problematic¹² because its presence is linked to Jahn-Teller distortion of the Na_xMnO_2 structure. More seriously, it is well demonstrated that Mn^{3+} is unstable and tends to produce Mn^{4+} and Mn^{2+} , which is readily soluble in conventional carbonate-based electrolytes¹¹⁻¹⁷. At high voltages (low Na content),

these soluble Mn ions may migrate into Na layers^{5,18} and then dissolve into the carbonate-based electrolytes along with the Na⁺ current¹¹⁻¹⁷. As a result, the dissolution of Mn ions contributes to irreversible structure evolution of the Na_xMn_{1-y}M_yO₂ cathodes, ultimately leading to a loss of active material^{11,19}. Moreover, once Mn²⁺ dissolves into the electrolyte, it migrates towards the anode driven by the electric field and the concentration gradient and finally deposits onto the anode surface^{20,21}. Such deposition severely degrades the SEI layer and accelerates the irreversible decomposition of the electrolyte¹¹.

Several research groups have attempted strategies to tame the dissolution of Mn including (1) raising the oxidation state of Mn by partially substituting Mn with lower valence state elements, such as Mg^{6,22,23}, Fe^{8,16}, etc^{9,24,25}; (2) modifying the surface of the cathode by coating a thin protective layer of MgO²⁶, Al₂O₃^{16,27}, graphene¹⁰, etc²⁸; and (3) the addition of electrolyte additives to form a passivation film on the cathode surface²⁹. However, most of these solutions inevitably lead to a capacity loss¹¹. Most recently, the Goodenough group applied a ceramic solid-state electrolyte to eliminate

the dissolution of Mn ions from the cathode, thereby improving the cycling capability of the Na battery¹². Also, it is known that some solid-state electrolytes (SSEs), including ceramics and polymers, are capable of delaying the growth of dendrites^{12,30-33}. This is also of crucial importance since the formation of dendrites is a significant challenge for metallic anodes (e.g. Li and Na), which can provide high theoretical specific capacity (3860 mAh/g and 1166 mAh/g for Li and Na, respectively³⁴) and high energy density. In spite of their promise, ceramic SSEs are brittle, difficult to process,³⁴⁻³⁶ and tend to poorly contact solid electrodes, limiting their usage to high temperatures (above 60 °C)^{35,37}. In contrast, composite-polymer electrolytes (CPEs)³⁸, with a polymer framework and ceramic fillers, are more flexible than Ceramic SSEs. Therefore, they have better contact with solid electrodes, facilitating operation at room temperature (RT)^{34,35,37}. A number of polymer hosts have been used in solid-state Na batteries (NBs), including PEO^{39,40} or PVDF-HFP⁴¹. However, PVDF with NASICON-type conductive ceramic fillers have not been reported yet. More significantly, the mechanism by which the CPE can stabilize both the cathode and anode of NBs has not been explored.

Here, we report, for the first time, that a solid-state CPE remarkably improves the cycle life of NBs by stabilizing both cathode and the metallic anode. In this study, the CPE consists of a PVDF matrix with NASICON-type $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NZSP) fillers and is denoted as PVDF/NZSP-CPE. A Mn-containing oxide, $\text{Na}_{0.67}\text{MnO}_2$ (NMO), is used as a model cathode to evaluate the performance of the PVDF/NZSP-CPE. We show that the cyclic stability and rate capability of the NBs are significantly enhanced if the PVDF/NZSP-CPE replaces the conventional carbonate liquid organic electrolyte (LOE). With the help of energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), and scanning electron spectroscopy (SEM), we show that the significantly improved cycle life is likely due to the presence of PVDF/NZSP-CPE, which (i) suppresses the dissolution of Mn ions from the NMO cathode; and (ii) delays the growth of the dendrites on the Na anode.

2. Results and Discussion

2.1 PVDF/NZSP-CPE Fabrication

NASICON-type NZSP was synthesized via a typical sol-gel method. The X-ray diffraction (XRD) pattern (Figure S1) clearly shows the monoclinic phase of the NZSP with a space group of C2/c, which is consistent with the literature⁴¹. The relatively sharp XRD signals and the good match between the observed and Rietveld-refined pattern (Figure S1) suggest that the NZSP is crystalline and free of impurities. PVDF/NZSP-CPE is composed of a PVDF matrix, NZSP fillers, and the sodium salt NaClO₄, as shown in Scheme 1.

Scheme 1. Schematic illustration of the PVDF/NZSP-CPE.

The characteristic peaks of NZSP could be observed from the XRD pattern of PVDF/NZSP-CPE (Figure 1a), revealing the presence of NZSP fillers. The other observed peak at 20.2° corresponds to the β -phase (110) plane reflection of PVDF⁴². The FTIR spectrum of PVDF/NZSP-CPE (Figure 1b) further confirms the existence of the β -phase of PVDF^{42,43} because of its characteristic peaks at around 843, 878, 1172, 1402, and 2980 cm^{-1} . As shown in Figure 1c and 1d, the as-fabricated PVDF/NZSP-CPE appears to be translucent, bendable, and freestanding with a thickness of 60 to $80\text{ }\mu\text{m}$ (Figure S1b).

Figure 1. (a) The XRD pattern of PVDF/NZSP-CPE and NZSP. (b) FTIR spectra of PVDF/NZSP-CPE. (c) and (d) digital photograph of PVDF/NZSP-CPE.

To investigate the impact of the NZSP fillers, a PVDF-based solid-state polymer electrolyte (PVDF-SPE) was also prepared using an identical method. The only difference is that we did not add NZSP ceramic fillers in the PVDF-SPE. Figure 2a and 2b show the scanning electron microscopy (SEM) images of PVDF-SPE and PVDF/NZSP-CPE. PVDF-SPE has a porous microstructure, while PVDF/NZSP-CPE

appears to be denser with fewer visible pores. We attribute the densification of PVDF/NZSP-CPE to the addition of NZSP fillers, the only different step in the preparation. A denser membrane is expected to improve the Na conductivity. The corresponding EDX maps in Figure 2c also suggest that Na, F, Zr, and Cl are evenly distributed in the PVDF/NZSP-CPE membrane. This elemental uniformity suggests that the NZSP fillers and Na salts are homogeneously dispersed in the PVDF framework.

The ionic conductivity of the PVDF/NZSP-CPE membrane was evaluated using electrochemical impedance spectroscopy (EIS) in a cell with an SS|CPE|SS (SS = stainless steel) configuration. EIS was carried out for a frequency range from 0.1 Hz to 1 MHz at room temperature (RT, 23 °C). The ionic conductivity σ is obtained using the following equation:

$$\sigma = \frac{L}{RA} \quad (1)$$

where R is the bulk resistance obtained from the Nyquist spectrum, L is the thickness of the solid electrolyte, and A is the nominal contact area between the SS

and the electrolyte. The electrochemical impedance spectra of SS|PVDF/NZSP-CPE|SS and SS|PVDF-SPE|SS cells are displayed in Figure 2d. The ionic conductivity of the PVDF/NZSP-CPE is estimated as 1.1×10^{-4} S/cm, while PVDF-SPE shows a one-order-of-magnitude smaller conductivity of 3.1×10^{-5} S/cm. This ionic conductivity improvement by the addition of NZSP fillers agrees with CPEs in previous reports³⁹⁻⁴¹ and is demonstrated as the result of (1) the interaction between the polymer and NZSP particles, which facilitates Na-ion mobility^{40,41} and (2) Na-ion hopping between Na-conducting NZSP particles^{40,41}.

Figure 2. SEM image of (a) PVDF-SPE and (b) PVDF/NZSP-CPE. (c) Energy-dispersive X-ray (EDX) spectra mapping of PVDF/NZSP-CPE. (d) Nyquist spectra of PVDF/NZSP-CPE and PVDF-SPE.

Electrochemical stability of the electrolytes is essential to make well-performing Na batteries. Figure 3a reports the RT linear sweep voltammograms (LSV) of PVDF/NZSP-CPE (sweep rate = 5 mV/s). As shown in Figure 2a, an oxidation current can be observed starting from 4.6 V vs. Na/Na⁺, while the current between 2.0

and 4.6 V is virtually zero. This result suggests that PVDF/NZSP-CPE is stable up to 4.6 V. Thermal stability is another important property of electrolytes. As shown in Figure 2b, the PVDF powder thermally decomposes at around 460 °C, consistent with the literature^{30,38}. If NZSP and NaClO₄ are added into the PVDF framework, the decomposition temperature lowers to about 360 °C, which is still much higher than that of conventional carbonate-based electrolytes (~100 °C)^{44,45} and ether-based electrolytes (~100 °C)⁴¹. This excellent thermal stability is beneficial to achieve highly safe Na batteries.

Figure 3. (a) Linear sweep voltammograms (LSV) curves of PVDF/NZSP-CPE. (b)

Thermogravimetric (TG) analysis of PVDF/NZSP-CPE and pure PVDF.

The electrochemical performance test of the PVDF/NZSP-CPE and a traditional

liquid organic electrolyte (LOE), 1 M NaClO₄/PC/5 vol% FEC, was conducted using CR2032 coin cells. To study the impact of the electrolytes on Mn-containing cathodes, Na_{0.67}MnO₂ (NMO) was used as the cathode (the loading was set at 1.2-1.5 mg/cm²). Na metal serves as the anode to investigate its compatibility with the PVDF/NZSP-CPE. The NMO|PVDF/NZSP-CPE|Na and NMO|LOE|Na cells are denoted as CPE-cell and LOE-cell, respectively. The resistances of the CPE-cell and LOE-cell were evaluated by electrochemical impedance spectroscopy (EIS) (Figure S2). The CPE-cell has a total resistance of 1050 Ω, a value much larger than the one recorded for the LOE-cell (143 Ω). Since the bulk resistance of PVDF/NZSP-CPE was measured to be 58 Ω (Figure 2a), the total resistance of the CPE-cell can be attributed to the large interfacial resistances. This interface problem is crucial in solid-state batteries, as it determines the Na insertion reversibility and the battery's capacity⁴¹. Therefore, to reduce the interfacial resistance of the CPE-cell, we modified the interfaces of NMO|PVDF/NZSP-CPE and PVDF/NZSP-CPE|Na by adding a small amount of LOE (1 M NaClO₄/PC/5 vol% FEC). The interface modified CPE-cells with 2 μl and 5 μl of LOE are denoted as CPE-2-cell and CPE-5-cell,

respectively. As shown in Figure S2, the total resistance of the CPE-2-cell and CPE-5-cell are measured to be 311 Ω and 280 Ω , respectively, much smaller than that of the original CPE-cell (1050 Ω). Additionally, we should note that this relatively small addition of LOE (2 μ l or 5 μ l) has little risk of ignition compared to traditional cells that contain 70 μ l to 100 μ l liquid electrolytes^{41,46}.

Figure 4a shows the galvanostatic charge and discharge profiles (second cycle) of four NBs at 0.2 C at RT. CPE-cell has a discharge specific capacity of 72.5 mAh/g, a value much smaller than that of LOE-cell (96.5 mAh/g). In contrast, the CPE-2-cell and CPE-5-cell have greater specific capacities of 95.6 mAh/g and 96.7 mAh/g, respectively. These two values are comparable with that of the LOE-cell (96.5 mAh/g). This capacity improvement may be ascribed to the lower interfacial resistances obtained by the interface modification.

Figure 4b displays the cyclic test of the NBs at 1 C after an initial 3 cycles at 0.2 C. Over 100 cycles, the discharge capacity of the LOE-cell decreased rapidly with a

decay of 0.50 mAh/g/cycle. The instability of the LOE-cell is in agreement with previously reported NBs using NMO as the cathode^{6,8,9,16,26}. In contrast, NMO|electrolyte|Na cells with PVDF/NZSP-CPE as the electrolyte (including the CPE-cell, CPE-2-cell, and CPE-5-cell) exhibit a much better cyclic stability. In particular, the cycling stability of the four NBs over 100 cycles (Figure 4b, c) follows the trend of CPE-cell (100 % capacity retention) > CPE-2-cell (94 % capacity retention) > CPE-5-cell (70 % capacity retention) > LOE-cell (45 % capacity retention). Interestingly, the smaller the LOE content, the higher the cell capacity retention is (Figure 4c). For instance, when the added LOE decreases (from 5 μ l to 2 μ l), the capacity retention is enhanced (from 70% to 94%). Therefore, the interface modification with LOE has both favorable and unfavorable consequences. On one hand, it improves the specific capacity, but, on the other hand, it accelerates the capacity decay. Although the CPE-cell shows the best cyclic stability, its specific capacity (Figure 4a) is relatively small due to the large interfacial resistance, indicating a trade-off between the specific capacity and the cyclic stability. The following discussion will focus on the CPE-2-cell because this battery has a relatively

large capacity and good cyclic stability.

Figure 3d shows the rate capability of the CPE-2-cell and the LOE-cell. It is obvious that the CPE-2-cell maintains a relatively large discharge capacity as the C rate is increased from 0.5 C to 4 C at RT. In contrast, an unstable discharge profile is observed for the LOE-cell. When the current density is higher than 1 C, the LOE-cell's capacity is lower than that of the CPE-2-cell, characterized by a steep decrease. Moreover, the CPE-2-cell's capacity goes back to 85.3 mAh/g when the C-rate is back at 1C. In contrast, the LOE-cell retains only 66.9 mAh/g. Both results indicate a superior rate performance of the CPE-2-cell over the LOE-cell.

Figure 4. (a) Galvanostatic charge and discharge profile at 0.2 C and (b) cyclic stability and coulombic efficiency at 1 C of the CPE-cell, CPE-2-cell, CPE-5-cell, and LOE-cell. The cycling tests were conducted after an initial 3 cycles at a 0.2 C rate. (c) Percentage of the initial discharge capacity retained (after 100 cycles) and LOE content versus cell type. (d) The rate performance of LOE-cell and CPE-2-cell.

To investigate the nature of the improved cycling stability and the superior rate capability of the CPE-2-cell, as compared to the LOE-cell, we conducted XPS and EDX, where we particularly tracked the dissolution of Mn from the NMO cathode.

Figure S4 shows SEM images of the cross-section of the glass fiber (GF) separator

used in the LOE-cell and the PVDF/NZSP-CPE used in the CPE-2-cell after cycling test (100 cycles at 1 C). As displayed in EDX mapping and EDX spectrum (Figure S4a), Mn is detected all over the GF, suggesting that some Mn ions of NMO are dissolved into the LOE during cycling. Moreover, for the LOE-cell, Mn ions are not only detected from the GF's cross-section, but also observed on the surface of the Na metal anode by both EDX (Figure 5a) and XPS (Figure 5c and 5d). This indicates that Mn ions leak from the cathode, dissolve into the LOE, and finally deposit on the anode. In comparison, for the CPE-2-cell, Mn is not detected even after 100 cycles in either the cross-section of PVDF/NZSP-CPE (Figure S4b) or the Na metal anode (Figure 5b and Figure S6). These data indicate that the PVDF/NZSP-CPE prevents the dissolution of Mn from NMO. This may be because the dissolution and migration of Mn ions in the SSEs are much more difficult compared to liquid electrolytes^{12,47}.

The deposited Mn species on the Na metal anode of the LOE-cell is analyzed by XPS (Figure 5c and 5d). As shown in Figure 5c, both the Mn 2p_{3/2} and Mn 2p_{1/2} peaks suggest the presence of Mn²⁺ and Mn³⁺ ions¹². The Mn²⁺ and Mn³⁺ ratios as calculated using Figure 4b are 74.28 % and 25.72 %, respectively. This result suggests that Mn²⁺

dominates the Mn-species deposited on the Na metal anode. A consistent result is obtained by analysis of the Mn 3s portion of the XPS spectrum (Figure 5d), where the separation energy (ΔE) between two peaks, which correlates with the average oxidation state of Mn, is measured to be 5.7 eV, a value corresponding to an Mn valence state slightly higher than 2.0^{48,49}. Therefore, Mn ions dissolved from the NMO cathode of an LOE-cell are mainly Mn^{2+} , in agreement with the literature^{11,13,14,16,17}. It is well demonstrated that the loss of Mn ions contributes to the capacity decay of the cathodes because (1) such a loss inevitably leads to irreversible decay of the cathode active material¹¹; and (2) the deposition of Mn^{2+} ions on the anode may destabilize the protective SEI film¹¹. Moreover, Figure 5e and 5f show the SEM images of the NMO cathodes after the cycling test. The NMO cathode of the LOE-cell appears looser (Figure 5e) with an observable gap between particles and the Al-foil current collector (Figure S7a). This suggests an irreversible shrink of the NMO particles during cycling, which may hinder the transfer of Na ions. On the other hand, the NMO cathode disassembled from the CPE-2-cell has a much denser morphology (Figure 5f and Figure S7b), indicating that the NMO particles do not

decrease in size. Further, the NMO particles appear to be well connected with the conductive carbon, PVDF binder, and current collector.

Figure 5. SEM images of Na metal anodes disassembled from (a) the LOE-cell and (b) the CPE-2-cell with insets reporting the EDX spectra of Mn. (c) the Mn 2p and (d) the Mn 3s portions of the XPS spectra detected at the Na metal anode of the LOE-cell.

SEM images of the NMO cathodes disassembled from (e) the LOE-cell and (f) the CPE-2-cell. All measurements were performed after the cycling test (100 cycles at 1 C).

In addition, another significant difference between the CPE-2-cell and the LOE-cell is the morphology of the Na metal anodes after cycling (Figure 5a and 5b). For the LOE-cell (Figure 5a), we can observe at the disassembled Na metal anode an uneven deposition of Na mimicking irregular dendrite-like structures. In contrast, the surface of the Na metal anode of the CPE-2-cell appears denser, much more uniform, and dendrite-free. Therefore, the application of the PVDF/NZSP-CPE in the CPE-2-cell not only prevents the dissolution of Mn ions from the NMO cathode, but also effectively lowers the risk of dendrite growth.

Although, dendrites are not observed for the CPE-2-cell, in agreement with many reported solid-state NBs^{12,47}, it is still unknown if the PVDF/NZSP-CPE is capable of completely suppressing the dendrites. In fact, recent research found that dendrites can

also grow in solid-state batteries and penetrate the SSEs when the current density is higher than a certain value, which is called the critical current density (CCD)^{50,51}. Therefore, to assess the compatibility between the PVDF/NZSP-CPE and Na metal, we assembled symmetric cells in a Na|electrolyte|Na configuration. Symmetric cells using PVDF/NZSP-CPE with and without the addition of 2 μ l of LOE are denoted as Na|CPE|Na and Na|CPE-2|Na, respectively. Figure 6a shows the time-dependent voltage profile of Na|CPE|Na and Na|CPE-2|Na at a current density of 0.2 mA/cm². Both Na|CPE|Na and Na|CPE-2|Na show stable voltage plateaus. However, after 350 h, a sudden voltage drop is observed with Na|CPE|Na, which may be caused by the growth of dendrites. In contrast, no sign of short circuit is observed for the Na|CPE-2|Na cell even after 1000 h, indicating that the growth of Na dendrites has been significantly delayed. Such improvement may be due to the improved interfacial contact between the Na metal and the PVDF/NZSP-CPE. Even though the PVDF/NZSP/Na is more flexible than ceramic SSEs, the contact between the PVDF/NZSP-CPE and the Na metal is still that between two solids. In this case, as illustrated in Figure 6c, the Na⁺ flux is unevenly distributed, and the local current

density is higher than the nominal one. In comparison, when the small voids between two solids are filled with a minute amount of LOE, more uniform pathways of Na^+ flux could be generated (Figure 6d), significantly improving the lifespan of Na|CPE-2|Na.

Figure 6. (a) The time-dependent voltage profile of Na|CPE|Na and Na|CPE-2|Na at a current density of 0.2 mA/cm^2 , while the insets show the expanded profiles. Schematic illustrating the Na^+ current distribution at the Na|PVDF/NZSP-CPE

interfaces (b) with and (c) without the interface modification.

3. Conclusion

In this study, a solid-state electrolyte, PVDF/NZSP-CPE, was fabricated and applied in the NMO|CPE|Na cells. After modifying the interface, the CPE-2-cell achieves a significantly better cyclic stability and rate capability than the LOE-cell while maintaining a similar discharge capacity. The superior performance of the CPE-2-cell could be ascribed to the following reasons. On the cathode side, the dissolution of Mn ions from the NMO cathode is eliminated by replacing LOE with PVDF/NZSP-CPE. On the anode side, the uneven deposition of Na and the growth of dendrites are significantly delayed by PVDF/NZSP-CPE. Moreover, the interface modification with a minute dose (2 μ l) of LOE improves the interfacial contact and uniforms the Na⁺ current. This work shows, for the first time, that a CPE can stabilize both the Mn-containing cathode and the Na metal anode, and thereby improve the cycle life of NBs. Therefore, this work provides possibilities of practical application of low-cost and highly safe solid-state NBs with enhanced performance.

4. Experimental Section

Na₃Zr₂Si₂PO₁₂ synthesis

The NASICON-type Na₃Zr₂Si₂PO₁₂ (NZSP) was prepared using a typical sol-gel method. Firstly, a solution containing tetraethyl orthosilicate, ethanol, and deionized water was prepared with a molar ratio of 1:10:20. Citric acid was then added to the solution under magnetic stirring at 60 °C. Stoichiometric quantities of NaNO₃, ZrO(NO₃)₂, and NH₄H₂PO₄ were dissolved into deionized water and then added to the previous solution. The solution was stirred at 80 °C until a white gel was formed. The gel was then dried at 150 °C before calcining at 450 °C for 5 h and 850 °C for 12 h. The resulting white powder was ball milled, pressed, and then sintered at 1200 °C for 24 h. Finally, the sintered pellet was cracked, and ball milled to obtain the NZSP powder.

Solid-state PVDF/NZSP-CPE preparation

Firstly, 0.45 g PVDF, 0.15 g NaClO₄, and 0.05 g NZSP were dissolved in 6 ml N-Methyl-2-pyrrolidone (NMP) under magnetic stirring at 60 °C until a homogeneous

solution was obtained. The solution was then dropped into a glass dish and dried at 80 °C for 24 h in a vacuum oven. The as-obtained semi-transparent membrane was cut into pieces (~20 mm) in a glove box. For comparison, a solid-polymer-electrolyte without NZSP (PVDF-SPE) was also prepared using an identical method. The only difference is that we did not add NZSP fillers in PVDF-SPE.

P2-type $\text{Na}_{2/3}\text{MnO}_2$ (NMO) synthesis

NMO was synthesized using a sol-gel method. Stoichiometric quantities of NaNO_3 and $\text{Mn}(\text{CH}_3\text{COO})_2$ were mixed with deionized water. Then citric acid was added to the solution and magnetically stirred at 80 °C until a clear gel was obtained. The gel was then dried in an oven at 150 °C, calcined in a box furnace at 450 °C for 5h, and finally at 950 °C for 12 h.

Physical characterization

The structure of NZSP, CPE, and SPE were identified by X-ray diffraction (XRD) with a PANalytical X'Pert Pro diffractometer with Cu K-alpha radiation and $\lambda = 1.5406 \text{ \AA}$. The morphology and elemental composition of the materials were observed by scanning electron microscopy (SEM) and energy dispersive X-ray

spectroscopy (EDX) using a JEOL-6700F instrument. X-ray photoelectron spectra (XPS) were acquired using a PHI5600 X-ray photoelectron spectrometer with a monochromatic Al X-ray source. The thermal gravimetric analysis (TGA) measurements were carried out on a TGA Q5000 instrument.

Electrochemical measurement

The ionic conductivity of the PVDF/NZSP-CPE membrane was estimated by electrochemical impedance spectroscopy (EIS) using an electrochemical potentiostat over a frequency range of 1 MHz to 0.1 Hz in an SS|PVDF/NZSP-CPE|SS cell (SS = stainless steel) at RT. The electrochemical potential window of PVDF/NZSP-CPE was studied by linear sweep voltammetry (LSV) using an SS|PVDF/NZSP-CPE|Na configuration. The electrochemical performance of PVDF/NZSP-CPE was evaluated by a battery test system (C2001A, LAND) with an asymmetric cell, which applied NMO as cathode and Na metal as the anode. The cathode was prepared by mixing NMO, Super-P carbon black, and PVDF with a weight ratio of 8:1:1 in the N-Methyl-2-pyrrolidone (NMP) solvent under magnetic stirring to obtain a viscous slurry. Then, the slurry was cast on a carbon-coated Al foil using a doctor blade and

dried in a vacuum oven at 80 °C for 24 h. The NMO loading on the cathode disc was calculated to be around 1.2 to 1.5 mg/cm². NMO|PVDF/NZSP-CPE|Na cells were charged and discharged under galvanostatic conditions in a voltage range of 2.5 V to 4.1 V at RT. All cells were CR2032 coin-cell-type and assembled in a glove box (Mikrouna, [O₂] < 0.1 ppm, [H₂O] < 0.1 ppm) filled with ultrapure Ar (99.999%, Air products).

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