# Sodiophilicity Regulation in Metallic Na Anodes

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The Na metal anode is the essential component for room-temperature sodium-metal batteries (SMBs), such as Na-S, Na-Se, and Na-$O_2$. However, the practical application of liquid-electrolyte-based SMBs has been troubled by extensive volume change and mossy/dendritic growth during Na electrodeposition. In this regard, the sodiophilicity (of the solid electrolytes or 2D/3D Na hosts) has been widely deemed vital for achieving stable Na metal anodes in either solid- or liquid-electrolyte-based SMBs, and many strategies have emerged to improve Na wettability and stabilize Na metal anodes for the three types of batteries.

sodium-metal batteries sodium-metal anodes Na wetting

## 1. Molten Sodium-Metal Batteries

Among the Na-based batteries considered for large-scale grid storage applications, molten sodium-metal batteries have recently regained popularity mostly due to the recent advancements in the development of intermediate-temperature molten sodium-metal batteries (SMBs), including Na-metal halide (Na-MH) and Na-S batteries based on a $\beta''$-$Al_2O_3$ solid electrolyte (BASE) [1][2][3][4][5][6]. BASE electrolytes have a high ionic conductivity (∼1 and 250 mS $cm^{-1}$ at 25 and 300 °C, respectively), an outstanding mechanical stability, and a wide electrochemical window. Unfortunately, they suffer from poor molten Na wetting, mandating the use of high temperatures (~300 °C) to ensure intimate Na|BASE interfacial contact and thus sufficient Na-ion conductivity [7]. It is of paramount significance to improve the molten Na wetting on BASE in order for intermediate-temperature molten SMBs to achieve further market penetration in grid applications.

Thus far, a great deal of promising and straightforward effort has been devoted to tackling this wetting challenge. Among the various strategies that have been proposed, the introduction of alloyable metallic coatings (e.g., Sn, Bi, In, Pb) or direct use of alloy anodes (i.e., Na-Cs alloy) on the BASE surface have proven effective [8][9][10][11][12][13]. For example, Lu et al. at PNNL reported a tactic of forming Na-K/Rb/Cs alloys that can markedly improve the wettability of liquid anodes on BASE [9]. The Na-Cs alloy anode shows much higher wettability on BASE than that of pure Na at various temperatures, achieving a perfect wetting (contact angle near 0°) at 250 °C. In light of computational modelling of the wetting process, the droplets can be observed to be reduced in height while expanded in breadth as the Cs content in the alloys rises. As a result, the Na-S cells with Na-Cs alloy anodes display only a slight capacity degradation when operated at 150 °C, delivering a capacity fade rate of <3% over 100 cycles. Even at a lower temperature (95 °C), the corresponding Na-Cs||S cells maintained a high capacity of 330 mAh $g^{-1}$ under a constant current of 7 mA (~C/7). Later, Chang et al. from the same group successfully enhanced Na wettability on BASE via a micron-sized Pb decoration realized by treating lead acetate trihydrate at 400 °C [10]. Benefiting from the formation of the Na-Pb alloy, a promising Na wetting phenomenon signified by the “sunny-side-up” shape was observed when Na droplets were placed on the BASE surface. Recently, Li et al. further improved the sodium wettability on BASE at 120 °C by raising the surface treatment temperature of lead acetate trihydrate and thus thinning the oxidation layer on Pb surface. The resulting low-temperature Na-S cell can reach a capacity as high as 520.2 mAh $g^{-1}$ and stable cycling over 1000 cycles [3]. In an effort to reduce the toxic Pb amount, the same group developed a coating on BASE consisting of a porous carbon network decorated with $PbO_x$ ($0 \leq x \leq 2$) nanoparticles [4]. An improved molten sodium wetting with a spreading temperature as low as 110 °C was achieved, along with ultrastable symmetric cell cycling for 6000 cycles at 120 °C. They found that sodiation could eventually break through the oxide shell and form metallic components at higher temperatures, as shown in Equation.

$$PbO, PbO_2 + Na \rightarrow Pb^0 + Na\text{-}Pb + \text{byproducts } (Na_2O)$$

Furthermore, this modification drastically lowered the Pb content to approximately 6 wt.% in the anode interface, and a complete elimination of the toxic Pb was also demonstrated by replacing Pb with environmentally benign Sn [4]. Some other impressive coatings have also been successful, such as iron oxide [14], various carbon-based modified materials [15][16], and Pt or Ni meshes [17][18].

In addition to BASE, NASICON-type solid electrolytes based on $Na_3Zr_2Si_2PO_{12}$ (NZSP), first proposed by Goodenough and Hong et al. in 1976, have also been applied in molten Na-metal batteries [19][20]. In the context of low temperature (<150 °C) molten SMBs, NASICONs exhibit higher ionic conductivities compared to BASE at low temperatures [19]. The poor Na wetting on BASE has been frequently ascribed to the high surface tension of molten Na and the formation of $Na_2O$ resulting from the reaction between molten Na and adsorbed water on the BASE surface, or to the presence of surface Ca impurities left over from synthesis [8][9][11]. However, few studies have been focused on improving the molten Na|NASICON interface, and it is unclear if such mechanisms and the abovementioned wetting-improving strategies for BASE can also be extended to NSICON solid electrolytes. To this end, Gross et al. greatly reduced interfacial resistance in sodium symmetric cells operated at 110 °C by an in situ formation of tin-based chaperone phases on NZSP surfaces. In combination with a well-designed revolutionary high-voltage NaI-$GaCl_3$ catholyte, the work enabled stable electrochemical cycling in a molten Na-NaI battery, sustaining more than 6000 h (>8 months) and 400 cycles with no discernible change in the voltage profile[21].

## 2. All-Solid-State Sodium-Metal Batteries

There have been quite a few interface engineering works so far aiming to enhance the Na|SE interfacial wettability, and most of them have been applied to NZSP-based solid electrolytes and only a few on BASE-based solid electrolytes [22][23][24][25][26], most likely due to the high room-temperature ionic conductivity (~1 mS/cm), ease of synthesis, and good chemical stability of NZSP [27][28].

The strategies to improve Na wettability on NZSP can be generally classified into two categories: (1) removing the surface passivation layer and (2) introducing sodiophilic wetting agents. The strategy (1) is mainly realized by mechanical polishing and high-temperature annealing designed to remove the NaOH/$Na_2CO_3$ surface contaminants on NZSP, thereby exposing the intrinsic NZSP surface with higher Na affability [29][30]. According to a recent work by Gao et al., by simply annealing NZSP at 450 °C for 2 h, the surface contamination layer can be effectively removed, leaving a clean and Na-deficient surface with much improved Na wettability (from a molten Na|NZSP contact angle of 122.5° to 72.5°) [29]. The strategy (2) involves multiple methods, including the implementation of Na-based composite anodes [31], surface coatings (i.e., Sn, $TiO_2$, $AlF_3$, PVDF, etc.) [32][33][34][35][36][37][38], and bulk doping of NZSP [39][40][41]. Zhou et al. demonstrated that heating NZSP over 300 °C results in the in situ formation of a thin interfacial interlayer with good molten Na wettability[30]. benefiting from the superior wetting and intimate interface contact of Na|H-NASICON, the interfacial resistance of Na||H-NASICON||Na is much lower than that of Na||NASICON||Na. The Na||H-NASICON||Na cell affords a steady cycle life up to 550 h at 0.15 mA $cm^{-2}$ and, subsequently, 0.25 mA $cm^{-2}$. The presence of stable voltage curves during long-term cycling implies the dendrite formation is suppressed owing to a better wetting of the interlayer.

Lu et al. proposed a trilayer monolithic Ca-doped NZSP pellet via a simple co-pressing method [39]. A porous|dense|porous trilayer structure was first constructed, and then a $SnO_2$ coating was applied by infusing $SnCl_4$ solution into the porous layers, followed by annealing at 500 °C in air. The resulting trilayer electrolyte achieved perfect molten infusion enabled by the capillary force and the sodiophilic $SnO_2$ coating. As a result, not only was the ingenious 3D porous electrolyte layer endowed with high ionic conductivity but it also reduced interfacial resistance. In light of these merits, the corresponding symmetric cell could be stably operated at room temperature for 600 h with low overpotentials under current densities ranging from 0.1 to 0.3 mA $cm^{-2}$ . Another common coating material, $TiO_2$, has been also applied to improve the NZSP|Na interfacial wettability. Gao et al. fabricated a two-phase composite NZSP ($TiO_2$) in which $TiO_2$ served as an additive [32]. $TiO_2$ is beneficial for the densification process because it contributes to reducing the sintering temperature, thereby preventing grain growth and encouraging a more uniform size distribution. The $TiO_2$ additive filled grain boundaries, as well as coated NZSP particle surfaces, improving molten Na wetting and mitigating dendrite growth. As a result, the $Na_3V_2(PO_4)_3$||NZSP($TiO_2$) ||Na cell delivered an outstanding rate performance and enhanced cycling stability in comparison to the NZSP cell . Recently, elemental metals alloyable with Na, i.e., Sn, were demonstrated to alleviate the Na|NZSP wetting issue. Oh et al. prepared a composite anode consisting of Na and $Na_{15}Sn_4$ by mixing Sn particles in molten Na [34]. Obviously, the $Na_5Sn$ composite showed higher wettability on NZSP owing to reduced surface tension and formed an intimate interfacial contact with no presence of pores. Furthermore, the presence of $Na_{15}Sn_4$ in the Na matrix improves the kinetics of interfacial Na transport, increasing vacancy diffusion and delaying pore formation at the anode-NZSP interface. Consequently, the robust $Na_5Sn$-NZSP interface underwent repeated galvanostatic cycling without failure for 300 cycles at 0.5 mA $cm^{-2}$.

Though relatively less studied, some interface engineering approaches were also reported to improve the Na|BASE wetting towards all-solid-state Na-metal batteries, i.e., introducing carbon- [22] and Sn-based materials [23][24][25], in which Sn was shown to be particularly effective in improving interfacial contact between Na and BASE. By depositing a thick Sn layer, the improved wettability of molten Na on BASE could be achieved, which is attributed to the decreased roughness and reduced surface tension of Na, and, more importantly, the formation of a $Na_{15}Sn_4$ alloy layer that is sodiophilic and can provide the necessary ionic/electronic conduction for Na plating/stripping [23]. Consequently, the symmetric cell using the modified BASE shows smaller voltage hysteresis and more stable galvanostatic cycling stability at 0.5 mA $cm^{-2}$. In an innovative manner, Lu et al. demonstrated a triple $Na_xMoS_2$-carbon-BASE nanojunction interface strategy to address the Na|BASE contact challenge [24]. With a rationally designed $Na_xMoS_2$-C-BASE triple junction interface, the adhesion between NA|BASE was dramatically improved, enabling high-capacity cycling of all-solid-state Na-S batteries at a low temperature of 80 °C, offering 500 mAh $g^{-1}$ after 50 cycles. A recent study by Deng et al. reported that an yttria-stabilized zirconia (YSZ)-enhanced BASE (YSZ@BASE) has an extremely low interface impedance of 3.6 Ω $cm^2$ with the Na metal anode at 80 °C, together with an extremely high critical current density of ~7.0 mA $cm^{-2}$. Furthermore, their quasi-solid-state Na||YSZ@BASE||$NaNi_{0.45}Cu_{0.05}Mn_{0.4}Ti_{0.1}O_2$ full cell achieves a high capacity of 110 mAh $g^{-1}$ with a Coulombic efficiency > 99.99% and retains 73% of the cell capacity over 500 cycles at 4 C and 80 °C. However, the work mainly highlights the stable $\beta$-$NaAlO_2$-rich solid-electrolyte interphase and strong YSZ support matrix that played a critical role in suppressing the Na dendrite instead of a wetting improvement [26].

## 3. Conventional Sodium-Metal Batteries

For conventional sodium-metal batteries using liquid electrolytes, the sodiophilicity regulation strategies was divided based on the types of host materials, including carbon-based hosts, alloy-based frameworks, and metal- and MXene-based skeletons.

### 3.1. Carbon-Based Hosts

Carbon cloths (CCs) are particularly appealing as scaffolds for advanced sodium-metal anodes because of their combination of mechanical toughness, electrical conductivity, low weight, and cost efficiency, which can effectively accommodate the volume deformation and mitigate dendrite growth during the Na plating/stripping procedure. Unfortunately, conventional CC is generally sodiophobic in nature and thus does not allow for the infusion of molten Na, motivating many modification approaches to introduce a desired sodiophilicity. Wang et al. developed a Na-carbon composite electrode with a sodiophilic matrix by employing a pre-heated CC and an infusion route, which allowed a homogeneous $Na^+$ deposition via a capillary action [42]. Similar to this strategy, Go et al. also fabricated nanocrevasse-rich Li/Na metal polyacrylonitrile (PAN)-based carbon composites [43], but a step closer comparison with the former was that large-scale Li/Na metal carbon composites can be fabricated with a simple machine. Aside from the studies mentioned above, it was widely reported that introducing alloy phases, metal oxide nanoparticles, functional groups, or heteroatom dopants could dramatically improve the sodiophilicity of CC, thereby significantly refining the stripping/plating behavior of Na metal anodes [44][45][46][47][48]. Recently, Wang et al. utilized a simple Na/In liquid immersion in a CC scaffold and a subsequent condensation procedure to synthesize a Na/In/C composite[44]. The existence of sodiophilic NaIn and $Na_2In$ phases on the Na/In/C composite electrode interface, as evidenced by experimental investigations and DFT simulations, is favorable to enhancing Na-ion deposition stability. When the Na/In/C anode was paired with the $Na_3V_2O_2(PO_4)_2F$ (NaVPOF) cathode, the full cell achieved a high specific capacity of 88.4 mAh $g^{-1}$ with a capacity retention of 87.6% after 800 cycles at 1 C rate. Ye et al.

prepared $RuO_2$@CC by a simple solution-based method [45]. After infusion of molten Na, the $RuO_2$@CC was converted to Na-Ru@CC anodes. The Ru nanoparticles not only played a role in assisting uniform $Na^+$ plating on the 3D carbon framework but reduced the local current density by offering high electrical conductivity. The Na-Ru@CC electrodes afforded a stable cycling over 250 h at 1 mA $cm^{-2}$ under a controlled capacity of 1 mAh $cm^{-2}$. Following a similar approach, Xiong et al. developed ultra-stable 3D-sodium-infiltrated $Fe_2O_3$-coated carbon textile anodes and sodium-infiltrated carbon textile (CT)-based anodes [46][47], both of which exhibited excellent machineabilities and stable cycling stabilities. In addition, a Co nanoparticle/N-doped carbon decorator (Co-VG/CC) was designed by Lu et al. via the approach[48]; the N-doped carbon could be simultaneously installed in the composite during the generation of Co nanoparticles, further enhancing the conductivity and sodiophilicity of Co-VG/CC.

Besides the CC-based sodium composite anodes, carbon papers (CP), carbon felts (CF), carbon sheets (CS), and carbon-fiber-based singles have also been adopted as hosts for sodium metal anodes. Similarly, the heteroatom dopants have been demonstrated effective in improving the surface wettability of the substrate, leading to uniform nucleation and deposition of Na metal. Zhao et al. rationally designed Na@CP-NCNTs composite electrodes by infiltrating Na into CP with N-doped carbon nanotubes (NCNTs) [49]. The growth of vertical NCNTs could successfully alter the Na wettability of CPs from “Na-phobic” to “Na-philic”. Therefore, the obtained Na@CP-NCNTs presented a homogeneous local current distribution and an intact 3D skeleton structure after repeated cycles. Nitrogen doping achieved by different N precursors (i.e., urea, melamine, ammonia, hexamethylenetetramine, polypyrrole, thiourea, etc.) has also been investigated but for other applications, such as supercapacitors and Li-ion batteries [50][51]. However, the potential influence of specific functional groups on sodiophilicity and their application in SMBs remain to be studied in depth. Later, Wu et al. successfully fabricated a Na-$Na_2S$-CTP (CTP: carbonized tissue paper) hybrid anode by filling sulfur-doped carbon networks with molten sodium [52]. The CTP defects generated during the sulfur doping process, as well as $Na_2S$ created on the surface of CTP, might lower mass transfer resistance and increase surface mobility during the sodium plating procedure. The alloying strategy could also improve the wettability of CF with Li/Na metal. Zhang et al. formed Li/Na-Sn alloys by introducing $SnO_2$ through a convenient solution-based method[53]. The surface energy between molten Li/Na and CF greatly decreased due to the as-formed Li/Na alloys, which enables even deposition of molten metal on the CF. The resulting Li/Na-Sn alloy layer could provide plenty of electrochemically active sites to drive uniform Li/Na nucleation and prevent dendrite formation. By introducing robust $Co_3O_4$ nanofibers onto a carbon sheet substrate, Zhao et al. constructed a hierarchical 3D $Co_3O_4$-CS scaffold with excellent wettability for alkali metal anode [54]. The 3D CS offers a primary framework with adequate Na nucleation sites, while Co/$Na_2O$ nanofibers provide physical incarceration of deposited Na and further reallocate the $Na^+$ flux on each carbon fiber. As a result, both Li/Na-Co-CS symmetrical cells exhibit glamorous lifespans with low overpotentials even at high current densities, which is due to the largely reduced local current density and minimal volume expansion. Distinctively, Chi et al. directed molten Na into unmodified carbon felt to fabricate Na/C composite electrodes [55].

Another carbon-based material, graphene, is a typical 2D framework that can effectively decrease the local current density and facilitate uniform Na deposition because of its large specific surface area, ultralight weight, and excellent adsorption in organic solvents. Wang et al. developed a processable and moldable Na@r-GO (r-GO:

reduced graphene oxide) composite anode using the molten Na infusion method, in which the GO (graphene oxide) is reduced to r-GO by contacting it with molten Na [56]. The as-obtained composite anode could be molded into various shapes and was stick-resistant. As expected, the plating/stripping behavior of the Na@r-GO composite anode was greatly prolonged electrochemically in both ether and carbonate electrolytes, with suppressed dendritic formation. Wu et al. created a robust ultra-light rGa (reduced graphene oxide aerogel) host by a hydrothermal reduction followed by oriented freeze-drying and transformation of rGa into Na@rGa via molten Na infusion [57]. Due to the advantages of ultra-light quality, uniform porous structure, and good wettability with both Na and electrolyte, the host endowed the Na@rGa composite anode with a high energy density and an excellent cycling performance in carbonate-based electrolyte without using any additives. Even at a high current density of 5 mA $cm^{-2}$, the Na@rGa composite anode could retain remarkable cycling stability with no dendrites and low hysteresis (50 mV) over 1000 cycles.

In efforts to inhibit the Na dendrite growth and improve the cyclability of Na metal anodes, other uncommon carbon material bodies (biomass, polymers, MOFs, etc.) have been investigated as effective hosts. Luo et al. prepared a Na-wood composite electrode via encapsulating metallic Na into porous channels within an electrically conductive carbonized wood host[58]. Most recently, Li et al. fabricated a 3D oxygen-containing carbonized coconut framework (O-CCF) from biomass waste coconut clothing [59]. Based on first principles and molecular dynamics simulations, a lone Na atom could be strongly adsorbed on O-CCF with C-O (2.04 eV) groups. Accordingly, the 3D O-CCF afforded to regulate the Na nucleation behavior and to prevent the Na dendrites growth, achieving an outstanding cyclability in Na-metal batteries. Even under brutal conditions of a high 5 mA $cm^{-2}$ with a fixed capacity of 10 mAh $cm^{-2}$, the O-CCF still realized a high coulombic efficiency of 99.6% over 1000 cycles. Liu et al. constructed a Na@CC skeleton via carbonization of cotton cloth, followed by molten Na infusion [60]. The successful N and O co-doping in CC not only reduced the local current density but also adjusted the uniform Na deposition. Recently, Liang et al. also demonstrated a nitrogen-doped hard carbon (NHC) composite electrode [61]. The N-functional groups modulated the surface chemistry of the hard carbon from sodiophobic to sodophilic, achieving the same effect as mentioned above: homogenizing the local electron distribution and physically preventing the formation of Na dendrites during the Na plating/stripping process. Mubarak et al. developed highly sodiophilic hollow and mesoporous carbon nanofiber (HpCNF) hosts with abundant defects and nitrogen functional groups through coaxial electrospinning[62]. Thanks to the uniform and reversible Na plating aided by the resilient fluorine-rich SEI layer, the Na@HpCNF anode in symmetric cell sustained more than 1000 h at 5 mA $cm^{-2}$ and a capacity of 5 mAh $cm^{-2}$. Tao et al. also reported a lignin-derived carbon nanofiber (LCNF) prepared by electrospinning to encapsulate molten Na [63]. The obtained self-sodiophilic LCNF host can evenly anchor the Na deposits and regulate SEI formation and was thus endowed with high cyclability. In generalized research, Zhu et al. discovered metallic sodium could be controllably deposited through main group II metals (Be, Mg, and Ba) owing to their definite solubilities in sodium [64]. In the case of the 3D hierarchical structure (3DHS) with Mg clusters, a superior “sodiophilic” affinity was observed. After Na infusion, their BET analysis showed that Na-3DHS presents a substantially smaller surface area (3.9 $m^2$ $g^{-1}$). Because of the abundance of Mg nucleation seeds, the nucleation barriers of sodium were markedly reduced by further homogeneously spreading Mg clusters in a three-dimensional hierarchical framework. Hence, The Na-3DHS exhibited great cycling stability, including a low overpotential of ~51 mV at 0.5 mA $cm^{-2}$ and 1 mAh $cm^{-2}$ after 100 cycles.

## 3.2. Alloy-Based Frameworks

Recently, “self-healing” liquid Na-K alloys at room-temperature have received more attention as promising Na metal anodes because of their ability to suppress dendritic growth while offering fast charge/discharge capability. However, due to high surface tension, the Na-K alloy anode not only prevents itself from spreading across the surface of the liquid electrolyte but also makes it extremely difficult to disseminate among hosts. What is more, the underlying chemistry of interface formation and carbon/Na-K interaction is still puzzling [65][66][67][68][69][70]. Xue et al. prepared a dendrite-free liquid Na-K anode by absorbing it into carbon paper at 420 °C and thoroughly investigated its dual-anode behavior [65]. The deciding factor for whether a liquid Na-K is a Na or K anode is the energy gained by the insertion of $K^+$ relative to $Na^+$; if the insertion of $K^+$ is more stable, $K^+$ is preferred over $Na^+$, but, if $K^+$ cannot be inserted, $Na^+$ is preferred. After that, Xue et al. utilized vacuum infiltration to immobilize a Na-K liquid alloy within porous membranes at an ambient temperature[66]. The experiment showed that the liquid anode membrane as obtained was compatible with all carbonate electrolytes but not with ether electrolytes. As a result, the Na-K-Al||$NaClO_4$||$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ cell presented an average coulombic efficiency of 99.8% with little capacity fade over 500 cycles at 1 C. In order to unlock the underlying chemistry involving interface formation and carbon/Na-K interaction, Zhang et al. reported an ultra-stable and high-capacity anode by using an in-situ-formed graphite intercalation compound (GIC) framework [67]. Designed as Na-K anodes, their unprecedented electrochemical properties could be showcased, which were associated with the synergy effect of fast electron and mass transport of the GIC networks, as well as self-healing behavior of the Na-K alloy. Xie et al. also showed a dendrite-free liquid metal anode made of CC@NaK composites [68]. In a similar manner, the $SiCl_4$ electrolyte additive was introduced in an ester-based electrolyte to construct a robust organic/inorganic hybrid interface on the Na-K liquid electrode by Wang et al. [69]. The $SiCl_4$ electrolyte additives not only serve as a physical barrier preventing highly reactive alloys from generation of $Na_2CO_3$ but also provided the benefit of fast charge-transfer kinetics. Dendrite-free electrochemical behavior was enabled by the hybrid interface connected to the hybrid interphase-modified Na-K (NKC-HI) electrode, as well as the inner liquid alloy. Consequently, the NVP/NKC-HI half cell exhibited a high capacity and outstanding rate performance, with a capacity retention of 103.6 mAh $g^{-1}$ after 1000 cycles at 2 C. Although extensive research indicated that the well-distributed deposits of liquid metal could be obtained owing to its “self-healing” characteristic, the mossy dendrites of Na still appeared suddenly when using somewhat extreme ratios of liquid Na-K. In this regard, Liu et al. demonstrated a dendrite-free NaK@Na anode by utilizing a liquid alloying diffusion mechanism [70]. Based on in situ optical imaging and theoretical prediction, the NaK@Na anode could deposit isotropically while avoiding dendrite formation.

In addition to the Na-K alloys matrix, some other metallic alloy strategies (Na-Sn and Na-Bi) can also be applied as a sodium metal anode. When compared to Na-K alloy matrix with high electronic conductivity (such as CC [69] or CP [65] host) or ionic conductivity (such as NVP host [71]), it is highly desired that the 3D hosts are both efficient in meeting ion and electron transportation pathways to effective uniform $Na^+$ deposition and prevent dendrite growth. Zheng et al. fabricated a percolated Na-Sn alloy/$Na_2O$ framework with dual ion/electron conductive pathways throughout the Na metal, the uniform, dendrite-free Na metal being realized during repeated $Na^+$ plating/stripping[72]. Top-view SEM images of NSCA-31 showcased a uniform, continuous Sn distribution within Na metal. DFT calculations revealed the Na-Sn alloy/$Na_2O$ framework was associated with a high “sodiophilicity” and a low $Na^+$ diffusion barrier. The result is that the NSCA-31 symmetric cell maintains excellent stability for up to 550 h under 2.0 mA $cm^{-2}$, with a capacity of 1.0 mAh $cm^{-2}$ . Afterwards, Cao et al. incorporated $SnO_2$@NZSP into bulk Na metal to obtain information about dendritic-free and stable BH-Na anodes [73]. As a devised hybrid anode, the NZSP functioned as fast $Na^+$ conduction, aiming to increase the reaction area of the whole electrode volume during plating/stripping of $Na^+$. Analogous to the above two cases, Ye et al. also constructed the periodic alternating of electron and ion conductivity in the 3D-$Na_3Bi$ alloy framework [74]. Furthermore, the 3D-$Na_3Bi$ alloy framework could effectively alleviate volume expansion, prevent side reactions with electrolyte, and hinder large dendrite formation due to its electron-conductive, ion-conductive, and sodiophilic nature.

## 3.3. Metal and MXene-Based Skeletons

For the purpose of confining molten Na within 3D current collectors so as to achieve a superior wettability and, in turn, even $Na^+$ deposition flux, some of the commercial porous metals (Cu foam, Al foam, Ni foam, and so on) have been used [66][75][76]. Wang et al. presented a composite Cu matrix as a stable host for effective impregnation with molten Na[75]. The unique surface property of the matrix could direct Na deposition from the scaffold toward the Na reservoirs within the pores, suppressing huge volume fluctuation and mossy/dendritic Na formation upon plating/stripping. The cycle stabilities of bare Na, Na@UCF, Na@S-CF, and Na@O-CF electrodes (UCF, S-CF, and O-CF, respectively, referred to untreated, S-treated, and O-treated Cu foams) in symmetrical cells at 0.5 mA $cm^{-2}$ with a capacity of 1 mAh $cm^{-2}$ were compared. It was obvious that the Na@O-CF delivered the smallest average overpotential of less than 50 mV and an outstanding cycle performance over 400 h. Clearly, the Na@O-CF electrode before and after 30 cycles also exhibited lower interfacial impedance values than Na@S-CF and Na@UCF. Recently, Xia et al. also constructed in situ a supersodiophilic 3D fluffy surface layer on a Cu foam host (SF-Cu-3.6) via a facile and controllable oxidation treatment strategy [76], and the Na/SF-Cu-3.6 composite anode delivered significantly better rate performance than that of a bare Na anode in $NaTi_2(PO_4)_3$-based full cells.

Recently, because of its abundant surface functional groups, high electronic/ionic conductivity, and high mechanical modulus, MXene, a remarkable two-dimensional (2D) layered material, has been intensively researched to regulate Li/Na deposition and inhibit dendritic growth [77][78][79]. Fang et al. ingeniously designed the Na-$Ti_3C_2T_x$-CC film composite, in which the $Ti_3C_2T_x$ functioned as sodiophilicity and fast electron channels, while the CC served as a durable skeleton to enable moldable and processable metal anodes[77]. According to first principles calculations and SEM observations, the protective mechanism of $Ti_3C_2T_x$ was realized by inducing an effective initial nucleation and producing “sheet-like” Na deposition inherited from the MXene architecture. Fang et al. also successfully prepared the 3D Li/Na-$Ti_3C_2T_x$-rGO films[78]. The abundant function groups existing on the $Ti_3C_2T_x$ surface contributed to good affinity between the $Ti_3C_2T_x$-rGO membrane and mixed covalent/ionic bonds (Ti-Li/Na, O-Li/Na, and F-Li/Na), leading to uniform electrochemical deposition and preventing dendritic puncture. The resultant Na-$Ti_3C_2T_x$-rGO electrodes presented a low overpotential of 20 mV after 800 h cycling at 1 mA $cm^{-2}$ and 1 mAh $cm^{-2}$. A hybrid rGO/MXene film was further introduced by Wang et al. [79], where the major advancement was that they realized an optimized N/P ratio of 3.8 in $Na_3V_2(PO_4)_3$||Na full cells, stretching the feasibility of their anode for practical sodium-metal batteries.

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