

Tailoring Chloride Solid Electrolytes for Reversible Redox

Phillip Ridley, George Duong, Sarah L. Ko, Jin An Sam Oh, Grayson Deysher, Kent J. Griffith,* and Ying Shirley Meng*

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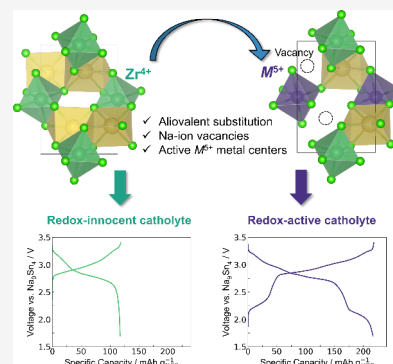
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ABSTRACT: Solid-state electrolytes enable next-generation batteries that can theoretically deliver higher energy densities while improving device safety. However, when fabricating cathodes for all-solid-state batteries, solid-state electrolytes must be combined with the active materials in high weight fractions in order to achieve sufficient ionic percolation within the cathode composite. This requirement drastically hinders the practicality of solid-state batteries as the solid-state electrolyte is conventionally designed to be electrochemically inactive and is effectively electrochemical “dead weight”, lowering both the gravimetric and volumetric energy density of the cell. In this work, a well-known solid-state electrolyte, Na_2ZrCl_6 , is modified by aliovalent substitution of inactive Zr^{4+} cations with redox-active M^{5+} ($M = \text{Nb}$ or Ta) cations to create a series of $\text{Na}_{2-x}M_x\text{Zr}_{1-x}\text{Cl}_6$ solid solutions that possess both high ionic conductivities and active sites for Na^+ storage. The Na^+ intercalation mechanisms of these solid-solution materials, in addition to those of the NaMCl_6 end-member materials, are elucidated in this work. It was discovered that both the niobium- and tantalum-containing chlorides exhibit rather high electrochemical potentials (2.2–2.8 V vs Na_0Sn_4), making them ideal catholytes to pair with commonly used oxide cathode materials like NaCrO_2 . This synergistic pairing leads to a cathode composite with an 83–102% increase in energy density and 39–81% improvement in areal discharge capacity compared to a redox-innocent solid electrolyte. This approach highlights the benefits of designing and employing redox-active solid-state electrolytes that can reversibly intercalate charge-carrying cations, opening up a broad new avenue for solid-state electrolyte discovery and solid-state battery design.



INTRODUCTION

Next-generation electrochemical energy storage technologies, such as solid-state batteries, have the opportunity to replace lithium-ion batteries only if they can offer improved safety and significantly enhanced energy density at competitive cost. Utilizing inorganic solid-state electrolytes may improve device safety if a cell experiences physical damage, while also enabling high-capacity anodes or anode-free cell configurations to attain substantial improvements in energy density.^{1–4} Furthermore, sodium-based chemistries, which make use of more abundant raw materials, present appealing cost and sustainability advantages and merit further development.^{5–7} Since the solid electrolyte is the principal component of a solid-state battery, its development is paramount in unlocking the pathway toward the commercialization of this technology. As such, we summarize the four key design criteria that classify an ideal solid electrolyte: (1) high ionic ($>10^{-4}$ S cm^{-1}) and low electronic ($<10^{-8}$ S cm^{-1}) conductivity, (2) sufficient mechanical pliability, (3) wide electrochemical stability, and (4) chemical compatibility with the active materials of choice. High ionic conductivity and good mechanical pliability are both necessary to fabricate a functional cathode composite, which typically consists of an active material—usually an oxide, a solid electrolyte, and an electronically conductive additive. These two properties allow for the fabrication of an electrode

composite with low porosity and high effective ionic and electronic conductivities (i.e., low tortuosity) by using a simple cold-press sintering method. Robust electrochemical stability of the electrolyte and chemical compatibility with the active material are both necessary criteria to maintain stable interfaces that enable highly reversible cycling and a long battery lifetime. However, to date, there is no single solid electrolyte material that meets all of the above criteria for a given battery system. As such, utilizing a bilayer design, which makes use of two separate solid-state electrolytes, such as using a chloride at the cathode and a borohydride at the anode, has been shown to be a promising approach for achieving exceptional electrochemical performance.⁴

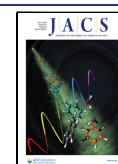
Since the first report of Li_3YCl_6 by Asano et al.⁸ in 2018, chloride solid electrolytes have emerged as promising materials for both lithium and sodium solid-state batteries due to their high ionic and low electronic conductivities, low Young's moduli, and unsurpassed electrochemical stability at high

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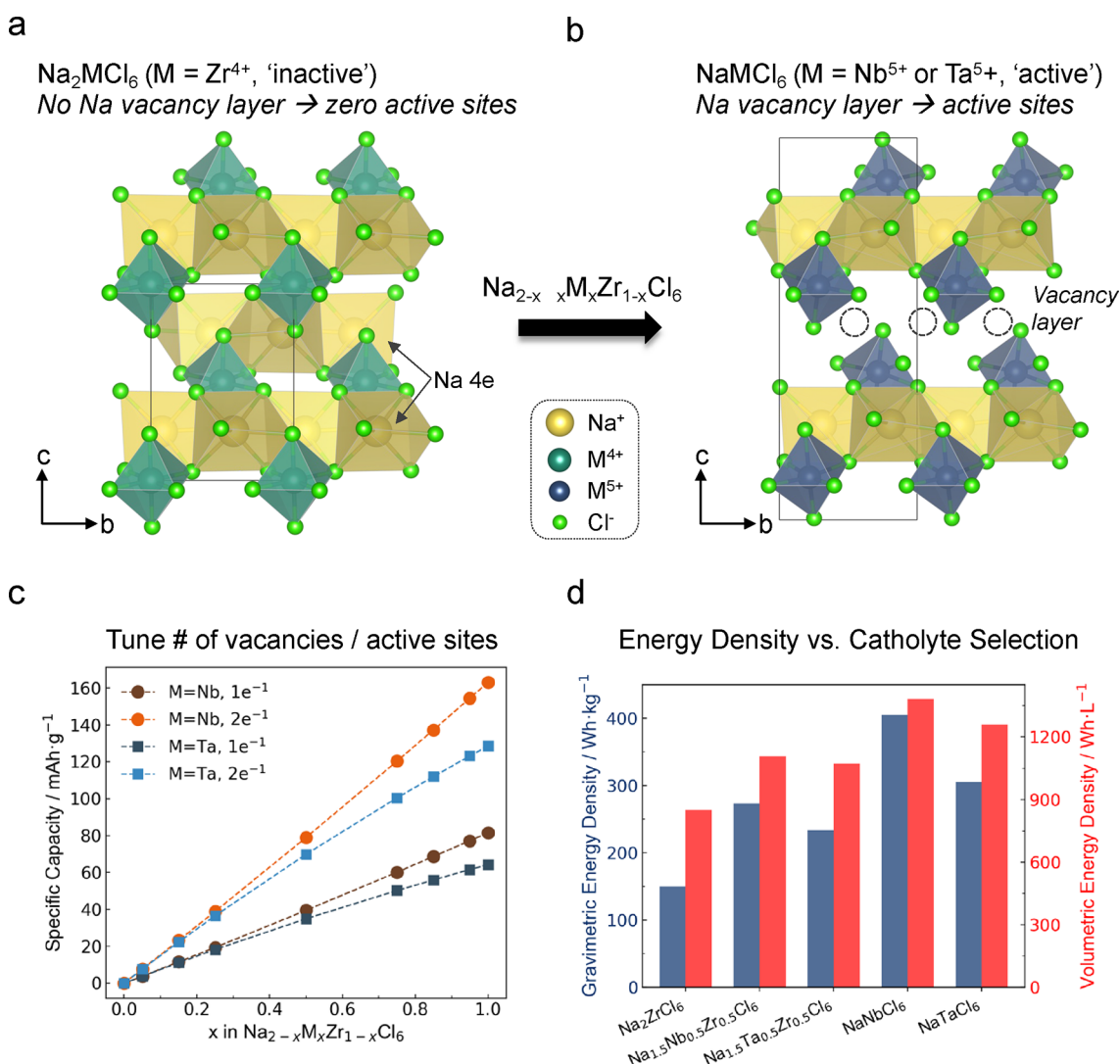


Figure 1. (a) End-member structures of Na_2MCl_6 ($M = \text{Zr}$) with fully occupied Na 4e sites and (b) NaMCl_6 ($M = \text{Nb}$ or Ta) with half of the Na 4e sites vacant forming a Na vacancy layer. (c) Tuning of Na 4e site vacancies to create active Na storage sites via aliovalent substitution of redox-active M^{3+} metal centers. (d) Cathode composite energy density using NaCrO_2 and redox-innocent and redox-active catholytes.

potentials. Notably, chlorides show the most promise as catholytes (i.e., electrolytes that are combined with positive electrodes), where they have been reported to be both chemically and electrochemically stable with numerous oxide-based cathode active materials, delivering excellent cycling performance without the need for protective coatings.^{8–10} However, ternary chloride phases exhibit lower ionic conductivities compared to state-of-the-art sulfides, like $\text{Li}_6\text{PS}_5\text{Cl}$. Na-ion conducting chloride analogues like $\text{Na}_3\text{M}^{3+}\text{Cl}_6$ ($M^{3+} = \text{Y}^{3+}, \text{Er}^{3+}, \text{In}^{3+}$), Na_2MCl_6 ($M = \text{Zr}^{4+}$), and NaMCl_6 ($M = \text{Nb}^{5+}, \text{Ta}^{5+}$), exhibit even lower ionic conductivities.^{10–15} $\text{Na}_3\text{M}^{3+}\text{Cl}_6$ compositions consisting of Y^{3+} or Er^{3+} as the immobile structural cation adopt a monoclinic $P2_1/n$ structure, with fully occupied Na 2e octahedral and Na 4e prismatic sites, resulting in very low ionic conductivity ($<10^{-6} \text{ S cm}^{-1}$). To overcome this transport bottleneck, aliovalent substitution has been demonstrated to be an effective approach to promote the vacancy-driven transport of sodium ions.^{11,12} Substituting M^{3+} ($M^{3+} = \text{Y}^{3+}$ or Er^{3+}) with Zr^{4+} cations leads to the formation of a series of $\text{Na}_{3-x}\text{M}_{1-x}\text{Zr}_x\text{Cl}_6$ ($M = \text{Y}^{3+}$ or Er^{3+} , $0 \leq x \leq 1$) solid-solutions with significantly enhanced ionic conductivity through

increased vacancy density on the octahedral Wyckoff 2e position. Another recent study elucidated the polymorphic nature of the Na_2ZrCl_6 end-member, revealing that $P3m1$ (minority phase) and $P2_1/n$ (majority phase) polymorphs are both formed via mechanochemistry and exist simultaneously in the resulting sample. Using a combination of ^{23}Na solid-state NMR, density functional theory, and X-ray diffraction measurements, it was shown that nonequilibrium synthesis methods, such as mechanochemistry, give rise to the metastable $P2_1/n$ polymorph. This structure, having one less mol of Na per formula unit than the Na_3YCl_6 end-member, results in the Wyckoff 2e position remaining vacant and accounts for its improved relative conductivity.¹⁶ More recent studies have reported on the ionic conductivity of the $\text{NaM}^{5+}\text{Cl}_6$ ($M^{5+} = \text{Nb}, \text{Ta}$) end-member structures and their solid-solutions with Zr^{4+} ($\text{Na}_{2-x}\text{M}_x\text{Zr}_{1-x}\text{Cl}_6$ ($M = \text{Nb}$ or Ta , $0 \leq x \leq 1$)) that demonstrate some of the highest room-temperature ionic conductivities ($>10^{-4} \text{ S cm}^{-1}$) among this class of materials to date. It was hypothesized that enhanced ionic conductivities in this system are due to inductive effects stemming from electronegativity differences between Zr, Nb, and Ta structural cations rather than the vacancy-driven

transport of Na-ions.¹⁵ Although many researchers have successfully improved on these four key design principles, achieving a truly energy-dense positive electrode requires a high active material content, which remains the glaring and unaddressed challenge for solid-state batteries.

Due to the higher density of chloride solid-state electrolytes ($\sim 2\text{--}3\text{ g cm}^{-3}$) compared to liquid electrolytes ($\sim 1\text{ g cm}^{-3}$), a large mass fraction of catholyte must be added, typically between 40–60 wt %, to reach a critical volumetric fraction where sufficient ionic percolation can be achieved while buffering capacity degradation arising from cathode–electrolyte contact loss.¹⁷ Doing so, while necessary, is a direct penalty for the energy density of the cathode. The solid electrolyte, by design, is electrochemically inactive and is therefore “dead weight”, which reduces energy at both the cathode and cell level. Solution-based infiltration methods have been proposed to partially reduce the mass fraction of solid electrolyte by achieving a thin uniform coating onto the surface of active material particles.^{18,19} However, this method requires chemical compatibility among the casted electrode, solid electrolyte, and chosen solvent, which limits the electrochemical systems where it can be applied. Moreover, mass fractions between 15–30 wt % of solid electrolyte are still necessary and result in lackluster cycling performance which may be improved with further optimization, although it is unclear to what extent improvement is possible. A completely different approach involves the incorporation of an electrochemically active solid electrolyte to nullify the “dead weight” issue.²⁰ The most effective way forward, in our view, necessitates a fundamental reevaluation of the catholyte’s function. Our approach involves tailoring highly conductive solid-state electrolyte crystal structures to possess reversible redox activity, with the goal of directly increasing the capacity delivered by the cathode composite electrode as a whole. Showcasing such an electrolyte aims to bring about a paradigm shift in solid-state electrolyte design, thus creating a fifth design criteria: (5) high catholyte specific capacity and voltage.

In this work, an aliovalent atomic substitution approach is applied to form a series of $\text{Na}_{2-x}\text{M}_x\text{Zr}_{1-x}\text{Cl}_6$ ($0 < x < 1$, $M = \text{Nb}$ or Ta) solid-solutions with Na_2ZrCl_6 ($x = 0$) and NaMCl_6 ($x = 1$, $M = \text{Nb}$ or Ta) as end-member structures, shown in Figure 1a. This approach aims to achieve two goals: (1) to enhance the ionic conductivity of Na_2ZrCl_6 and NaMCl_6 end-member structure and (2) to activate redox-innocent Na_2ZrCl_6 by incorporating redox-active Nb^{5+} or Ta^{5+} to trigger charge storage capacity in a conventionally dead weight component. The emergence of catholyte capacity is shown in Figure 1b while its impact on the practical energy density of the electrode composite is highlighted in Figure 1c. Moreover, the electrochemical charge storage properties of the NaMCl_6 end-member structures are also reported. Lastly, the materials discussed in this work are prepared through a simple mechanochemical synthesis approach, where binary metal chloride precursor powders (NaCl , ZrCl_4 , NbCl_5 , and TaCl_5) are mixed in stoichiometric quantities and ball milled to yield solid electrolyte powders. The study demonstrates that not only can the energy density of practical solid-state batteries be improved but also it can be achieved in a cost-effective manner, which is crucial for the broader adoption of solid-state batteries.

METHODS

Solid Electrolyte Synthesis. All $\text{Na}_{2-x}\text{M}_x\text{Zr}_{1-x}\text{Cl}_6$ ($M = \text{Nb}$ or Ta ; $x = 0.25, 0.5, 0.75$) solid-solutions were prepared in an inert, Ar-rich glovebox (MBRAUN MB200B: $\text{H}_2\text{O} < 1.0\text{ ppm}$ and $\text{O}_2 < 1.0\text{ ppm}$) using stoichiometric amounts of anhydrous NaCl (Sigma-Aldrich, $\geq 99\%$), TaCl_5 (STREM, 99.99%), NbCl_5 (STREM, 99.99%), and ZrCl_4 (STREM, 99.95%). The powders were weighed using an analytical balance (Ohaus Pioneer) and hand mixed with a mortar and pestle in batch sizes of 1 g. Mixtures were then transferred into 50 mL zirconia-lined ball milling jars loaded with 30 g of 5 mm zirconia milling media. The samples were ball milled (Retsch Emax) for 10 h at 500 rpm in 15 min milling intervals, followed by 1 min rest periods.

Electrochemical Measurements. Electrochemical Impedance Spectroscopy (EIS). Ionic conductivities for all electrolyte samples were calculated from Nyquist plots obtained using an applied voltage of 10 mV and a frequency range of 1 Hz to 1 MHz using a BioLogic SP-300. An AB/SEIAB (AB = acetylene black) symmetric cell was constructed by filling a 10 mm-diameter polyether ether ketone (PEEK) die with 100 mg of solid electrolyte powder, which was pelletized with two Ti plungers at 310 MPa using a hydraulic press (Carver). The Ti plungers were removed, and approximately 2 mg of acetylene black was densified to 250 MPa on both sides of the pellet to provide better contact and act as the current collector. The symmetric cell was secured to a holder that applied a stack pressure of approximately 70 MPa.

Direct-Current Polarization (DCP). Electronic conductivities for all electrolyte samples were extracted from direct-current polarization tests performed by using a Solartron 1260 impedance analyzer by applying a potential of 0.05 V for 600 s. Symmetric cells used to perform DCP measurements were prepared identically to those used for EIS.

Linear Sweep Voltammetry (LSV). Oxidation and reduction stabilities for all electrolyte samples were explored using linear sweep voltammetry from 0–6 V vs Na_9Sn_4 . A positive electrode composite consisting of 96% $\text{Na}_{2-x}\text{M}_x\text{Zr}_{1-x}\text{Cl}_6$ ($M = \text{Ta}$ or Nb ; $x = 0.25, 0.5, 0.75$) solid electrolyte and 4% vapor-grown carbon fiber (VGCF) was formed via hand-mixing in a mortar and pestle. A pellet cell was assembled in a 10 mm diameter PEEK die via densification with a hydraulic press (Carver) using two Ti plungers as current collectors. First, a bilayer electrolyte separator consisting of 20 mg $\text{Na}_4\text{B}_{10}\text{H}_{10}\text{B}_{12}\text{H}_{12}$ (NBH) and 50 mg of $\text{Na}_{2-x}\text{M}_x\text{Zr}_{1-x}\text{Cl}_6$ was formed via densification at 125 MPa. About 12 mg of positive electrode composite was added on top of the $\text{Na}_{2-x}\text{M}_x\text{Zr}_{1-x}\text{Cl}_6$ layer while 35 mg of the Na_9Sn_4 negative electrode was below the NBH layer. The cell was then densified at 370 MPa and attached to a holder. Separate LSV measurements were performed scanning from open-circuit voltage (OCV) to 0 V for reduction and from the OCV to 6 V for oxidation at a rate of 0.100 mV/s on a BioLogic SP-300 under inert conditions and at room temperature.

Battery Testing. Electrochemical performance was examined by constructing half-cells using a NaCrO_2 (NCO) positive electrode, a Na_9Sn_4 negative electrode, and an NBH electrolyte separator. To incorporate $\text{Na}_{2-x}\text{M}_x\text{Zr}_{1-x}\text{Cl}_6$ ($M = \text{Tma}$ or Nb ; $x = 0.25, 0.5, 0.75$) electrolytes, a positive electrode composite was hand mixed using a mortar and pestle at a weight ratio of 40:58:2 of NCO:NMZC:VGCF. A pellet cell was assembled in 10 mm-diameter PEEK die via densification with a hydraulic press (Carver) using two Ti plunger current collectors. First, 40 mg of NBH powder was pressed to 125 MPa, followed by 35 mg of Na_9Sn_4 pressed to 370 MPa. Finally, approximately 12 mg of NCO composite was added to the opposite side and pressed to 370 MPa. The battery was secured to a cell holder and connected to an electrochemical cycler (Landhe) programmed to cycle 3 times at C/3, followed by C/10 cycling at room temperature in an Ar-rich glovebox.

X-ray Diffraction Measurements. Solid electrolyte powders were loaded into 0.5 mm-diameter boron-rich glass capillary tubes (Charles Supper Company) while inside an Ar-filled glovebox. The tubes were sealed with clay, transferred out of the glovebox, and flame-sealed

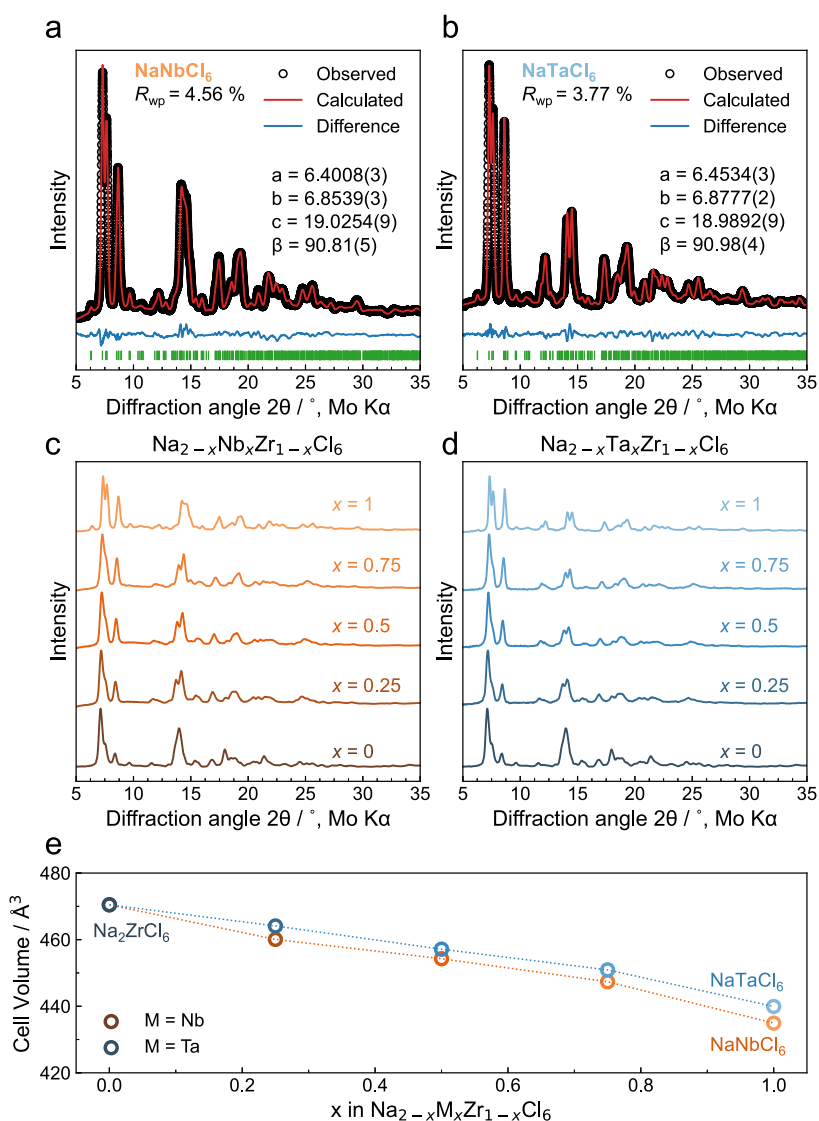


Figure 2. Rietveld refinement of (a) NaNbCl₆ and (b) NaTaCl₆ end-members. X-ray diffraction patterns of (c) Nb-substituted and (d) Ta-substituted Na_{2-x}M_xZr_{1-x}Cl₆ (M = Nb, Ta) solid-solutions. Unit cell volumes belonging to respective Na_{2-x}M_xZr_{1-x}Cl₆ (M = Nb, Ta) compositions were calculated from lattice constants that were determined from Le Bail fits. Estimated standard deviations were too small to be graphically represented and are omitted.

with a butane torch to create a hermetic seal. XRD patterns were collected over a 5–50° 2θ range with an integration step size of 0.01° using a Bruker X8-ApexII CCD sealed tube diffractometer equipped with a molybdenum radiation source ($\lambda_{\text{Mo}} = 0.7107 \text{ \AA}$). Le Bail fitting and Rietveld refinements were conducted using GSAS-II.²¹

Solid-State NMR Spectroscopy Measurements. All solid-state NMR measurements were conducted at 9.4 T with a Bruker Ascend 400 magnet, a Bruker Avance NEO NMR spectrometer, and a 5.0 mm Phoenix HX probe. Powder samples were center-packed between PTFE tape plugs under an inert Ar environment in zirconia rotors with PCTFE and polyimide caps. 1D measurements were collected using a direct pulse–acquire sequence and a recycle delay time of $\geq 5 \times T_1$ for the longest T_1 , which was that of the sodium chloride impurity. T_1 (longitudinal) relaxation was measured with a saturation–recovery sequence with up to 33 delay times spanning 10 μs up to 1000 s, equally spaced in $\log_{10}(t)$. ²³Na spectra were measured at a Larmor frequency of 105.84 MHz and under a magic angle spinning (MAS) frequency of 8 kHz (no temperature regulation). ²³Na was referenced to solid NaCl at 7.21 ppm.²² 1D spectra were recorded with a 45° pulse of 1.5 μs (83 kHz). ⁹³Nb spectra were measured at a Larmor frequency of 97.83 MHz under 8 kHz MAS. 1D spectra were recorded with a pulse of 1.0 μs , which is estimated to be

a 30° pulse based on the liquid-phase 90° pulse of the nearby ¹³C. 1D ²³Na and ⁹³Nb spectra were fit with either Gaussian/Lorentzian line shapes or a second-order quadrupolar interaction model under MAS using the Dmfit software package.²³ Calculated NMR tensors were computed on DFT-optimized structures that were geometry optimized using the LBFGS scheme in the CASTEP v23.1 planewave DFT code until forces on atoms were less than 0.01 eV/Å and the maximum stress was lower than 0.1 GPa.²⁴ Starting structures were taken from experimental models fit to powder X-ray diffraction data. NMR parameters were calculated with the gauge-including projector augmented wave (GIPAW) method.²⁵ All calculations used a Monkhorst–Pack²⁶ k -point grid with a spacing of $2\pi \times 0.04 \text{ \AA}^{-1}$, a planewave cutoff energy of 600 eV, and on-the-fly ultrasoft pseudopotentials generated within CASTEP with the PBE²⁷ exchange–correlation functional. Spectral simulations in the figures were obtained by first simulating the GIPAW calculated values and then refining the isotropic chemical shift and the quadrupolar coupling magnitude and asymmetry to obtain a best fit of the simulation to the experimental data.

XAS Measurements. Transmission XAS measurements were acquired at the Zr K-, Nb K-, and Ta L₃-edges using beamline 6-BM of the National Synchrotron Light Source II (NLSL-II). Samples

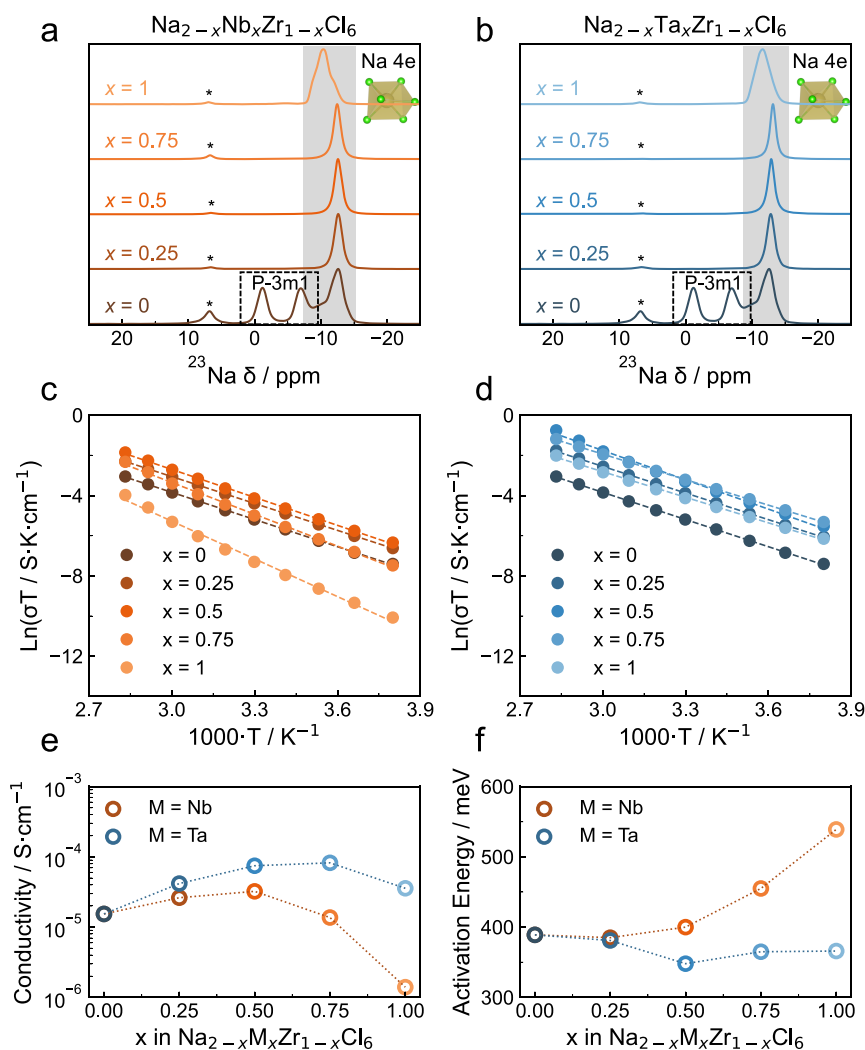


Figure 3. (a, b) ^{23}Na Solid-state NMR spectra at 9.4 T and 8s kHz MAS rate, (c, d) Arrhenius plots, (e) ionic conductivity measurements, and (f) fitted activation energy values for Nb-substituted (orange) and Ta-substituted (blue) $\text{Na}_{2-x}\text{M}_x\text{Cr}_{1-x}\text{Cl}_6$ (M = Nb or Ta) solid-solutions. Asterisks (*) correspond to NaCl.

were prepared by diluting and mixing pristine or sodiated $\text{Na}_{2-x}\text{M}_x\text{Cr}_{1-x}\text{Cl}_6$ (M = Nb or Ta; $x = 0, 0.25, 0.5, 0.75, 1$) powders with carbon and PTFE binder to achieve a targeted edge jump of approximately 0.5–1 for each respective edge of interest. To ensure that the prepared samples were flat and uniform, the mixtures were densified at 250 MPa using a hydraulic press (Carver) and a 10 mm pellet press die set. The Zr and Nb data sets were energy-calibrated to the main edge of Zr and Nb metal foil standards (calibrated to 17.998 and 18.986 keV, respectively). The Ta data sets were energy-calibrated to the main edge of a Ta oxide standard, Ta_2O_5 (9.86 keV). Data sets consisted of 3–12 scans, which were then averaged. Data normalizing was done using the Athena software package and EXAFS fitting was done using k^3 -weighted experimental $\chi(k)$ data and FEFF6 within the Artemis software package.²⁸

RESULTS AND DISCUSSION

X-ray diffraction patterns recorded at 293 K for mechanochemically synthesized NaMCl_6 (M = Nb or Ta) end-members (Figure 2a, b) reveal that such compositions adopt the monoclinic $P2_1/c$ structure, which has previously been reported for the same compositions synthesized via solid-state reactions.²⁹ Rietveld refinements were carried out using NaNbCl_6 (ICSD #36518) and NaTaCl_6 (ICSD #36519) as starting models. Lattice constants, atomic coordinates, and

isotropic thermal displacement parameters were freely refined (Figure 2, crystallographic data shown in Supplementary Tables S1 and S2). No diffracted intensity from NaCl or MCl_3 precursors could be observed. Moreover, the inclusion of such impurities did not influence the fitting result in any meaningful way, indicating that the NaNbCl_6 and NaTaCl_6 samples obtained via mechanochemistry are phase-pure, but, as will be highlighted by NMR spectroscopy (*vide infra*), may possess negligible amounts of impurity (<2 wt %) that are outside of the detection limits of XRD. On the other hand, the Na_2ZrCl_6 end-member adopts a similar monoclinic $P2_1/n$ structure but retains two moles of Na^+ per formula unit that occupy prismatic sites in the 4e Wyckoff position. Previous studies revealed that its crystallography is more complicated when utilizing nonequilibrium synthesis methods such as mechanochemistry. Specifically, while the $P\bar{3}m1$ polymorph is energetically favored, ball milling gives rise to a majority fraction of metastable $P2_1/n$, which agrees with our two-phase Le Bail fitting result here (Supplementary Figure S1).¹⁶ Interestingly, all blended $\text{Na}_{2-x}\text{M}_x\text{Cr}_{1-x}\text{Cl}_6$ (M = Nb or Ta; $0.25 \leq x \leq 0.75$) compositions were found to form solid-solutions adopting the same monoclinic $P2_1/n$ structure as the Na_2ZrCl_6 end-member without the presence of any additional

adventitious peaks (Figure 2c and Figure 2d). Le Bail refinements (Supplementary Figures S2 and S3) further confirm the formation of solid-solution phases, showing a monotonic decrease in lattice constants (Supplementary Figure S4) as the degree of M^{5+} substitution approaches the NaMCl_6 ($M = \text{Nb}$ or Ta) end-member. The contraction of lattice constants is attributed to differences in ionic radii ($\text{Zr}^{4+} = 72$ pm, $\text{Nb}^{5+} = 64$ pm, and $\text{Ta}^{5+} = 64$ pm) and increased Na 4e site vacancy concentration that allow $[\text{MCl}_6]^-$ octahedra to pack more closely. Accordingly, a monotonic but nonlinear decrease in cell volume is observed going from Na_2ZrCl_6 to the NaMCl_6 end-members (Figure 2e), similar to what has been observed for other chloride solid-solutions of the same space group.^{12,15} Due to the high-energy ball milling synthesis conditions, the diffraction patterns exhibit some peak broadening, which likely arises from crystallite size and microstrain broadening effects resulting from repeated particle fracturing, which reduces domain size and induces defects. However, further analysis of such effects and full Rietveld refinements were not carried out due to instrumental limitations.

^{23}Na solid-state NMR measurements were carried out on all $\text{Na}_{2-x}\text{M}_x\text{Zr}_{1-x}\text{Cl}_6$ ($M = \text{Nb}$ or Ta ; $0 \leq x \leq 1$) compositions, with spectra acquired for the Nb-substituted series shown in Figure 3a, and the Ta-substituted series shown in Figure 3b. Small quantities (0.1 to 1 wt %, Supplementary Table S3 and S4) of NaCl impurity (7.2 ppm) were observed in all samples, which is in good agreement with XRD results and provides further evidence for the high purity of the synthesized phases. In the Na_2ZrCl_6 end-member, there are two octahedral environments (0 to -5 ppm) attributed to the Na 6h and 6g sites of the $P\bar{3}m1$ polymorph and a single prismatic site (-11 ppm) attributed to the Na 4e site of the $P2_1/n$ polymorph.¹⁶ On the other hand, $\text{Na}_{2-x}\text{M}_x\text{Zr}_{1-x}\text{Cl}_6$ ($M = \text{Nb}$ or Ta ; $0.25 \leq x \leq 1$) compositions exhibit a single resonance at -11 to -13 ppm, which is attributed to the Na 4e prismatic site of the $P2_1/n$ structure. Simulated solid-state NMR spectra were refined using parameters obtained from first-principles calculations and show good agreement between the experimentally fitted results and calculations (Supplementary Figure S6 and Supplementary Table S5). In addition, ^{93}Nb spectra for raw $\text{Na}_{2-x}\text{Nb}_x\text{Zr}_{1-x}\text{Cl}_6$ ($0.25 \leq x \leq 1$) and simulated NaNbCl_6 are shown in Supplementary Figure S7 and Supplementary Table S6. Interestingly, ^{23}Na NMR measurements reveal broader quadrupolar line shapes for the NaNbCl_6 and NaTaCl_6 end-members, while narrower Gaussian line shapes were observed for all Nb- and Ta-substituted compositions despite the fact that more unique local environments and larger polyhedral distortions are expected within the solid-solution series. T_1 measurements indicate a drastic reduction in relaxation time ranging from several seconds to tens of milliseconds (Supplementary Table S7) going from the NaMCl_6 end-member to solid-solutions, suggesting improved Na-ion mobility. Therefore, it is likely that a motional averaging effect due to fast chemical exchange between Na 4e sites contributes to the observed narrow Gaussian line shapes of the solid-solution compositions.

Conductivity measurements and Arrhenius plots, shown in Figure 3c and 3d, provide insights into the impact of the substitution degree (i.e., x in $\text{Na}_{2-x}\text{M}_x\text{Zr}_{1-x}\text{Cl}_6$) on ionic conductivity and activation energy. Electronic conductivity measurements were also carried out using the direct-current polarization method, shown in Supplementary Figure S5, and revealed that all Na-M-Zr-Cl ($M = \text{Nb}$, Ta) compositions are

poor electronic conductors. The trend between ionic conductivity (at 30°C) and degree of substitution was examined, with results shown in Figure 3e and 3f. In the case of the Nb-substituted solid-solution series, the measured ionic conductivity increases as Nb^{5+} cations are first introduced into the $P2_1/n$ structure, the conductivity reaches a maximum value of $3.2 \times 10^{-5} \text{ S cm}^{-1}$ at the $x = 0.5$ composition ($\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$), and decreases as the concentration of Nb^{5+} increases further, reaching $1.4 \times 10^{-6} \text{ S cm}^{-1}$ at the NaNbCl_6 end-member composition. Similarly, for the Ta-substituted solid-solution series, the ionic conductivity increases with the substitution of Ta^{5+} into $\text{Na}_{2-x}\text{Ta}_x\text{Zr}_{1-x}\text{Cl}_6$. However, in this case, a maximum conductivity of $8.2 \times 10^{-5} \text{ S cm}^{-1}$ is observed at the $x = 0.75$ composition ($\text{Na}_{1.25}\text{Ta}_{0.75}\text{Zr}_{0.25}\text{Cl}_6$), with the ionic conductivity dropping slightly to $3.6 \times 10^{-5} \text{ S cm}^{-1}$ for the end-member NaTaCl_6 . Interestingly, while the ionic conductivity of the NaTaCl_6 end member is $\sim 2x$ higher than the Na_2ZrCl_6 ($1.5 \times 10^{-5} \text{ S cm}^{-1}$) end-member, the NaNbCl_6 end-member is an order of magnitude lower. Several possible explanations are considered. First, the charge carrier concentration and vacancy density likely play a role. As the concentration of M^{5+} substituents increase, the number of Na^+ per formula unit decreases, while the Na 4e site vacancy increases. Unlike the Na_3YCl_6 end-member, which possesses an additional mole of Na^+ per formula unit, the Na 2e octahedral site remains vacant in all $\text{Na}_{2-x}\text{M}_x\text{Zr}_{1-x}\text{Cl}_6$ ($M = \text{Nb}$ or Ta ; $0.25 \leq x \leq 1$) compositions, as evidenced by ^{23}Na solid-state NMR measurements. The introduction of sodium vacancies on the 4e site may further promote Na^+ diffusion by lowering activation barriers, which has also been observed for $\text{Na}_{3-x}\text{Er}_x\text{Zr}_{1-x}\text{Cl}_6$ solid-solutions and other sulfide Na^+ conductors.^{12,30,31} Additionally, the incorporation of M^{5+} metal cations effectively ‘stabilize’ the $P2_1/n$ structure leading to phase-pure solid-solutions, resulting in an effective removal of the less conductive $P\bar{3}m1$ polymorph that is present in Na_2ZrCl_6 . Second, NaTaCl_6 has a larger unit cell compared to NaNbCl_6 . While Ta^{5+} and Nb^{5+} have similar ionic radii, this difference can be attributed to the longer average Na–Cl bond length observed in NaTaCl_6 compared to NaNbCl_6 (2.88 vs 2.77 Å, obtained from Rietveld refinement), resulting in enlarged spacing of the $[\text{MCl}_6]^-$ framework. This suggests that there is a weaker interaction between Na^+ and Cl^- in NaTaCl_6 than in NaNbCl_6 , which may be the reason for its comparatively higher ionic conductivity in the former. Lastly, the inductive effect has been shown to play a significant role in ionic conductivity for sulfides and similar chloride chemistries.^{15,32} However, this explanation may not sufficiently capture the differences in chemical bonding between Ta–Cl and Nb–Cl. Both the Na^+ vacancy density and M–Cl bonding likely play a role and ultimately determine the measured ionic conductivity. In the case of the Nb-substituted solid-solutions, there is an increase in ionic conductivity upon Nb^{5+} substitution due to increased Na 4e site vacancies lowering the activation barrier, but this increase in conductivity is lost as the concentration of Nb^{5+} cations incorporated into the structure increase. This likely results from lower Na^+ mobility arising from stronger interactions between Cl^- and Na^+ , which is a consequence of the higher electronegativity in the case of Nb compared to that of Zr. On the other hand, the Ta-substituted solid-solutions exhibit ionic conductivities that continue to increase to higher Ta^{5+} concentrations, likely due to increased Na 4e site vacancies and weaker interactions between Na^+ and Cl^- . Moreover, it should also be noted that

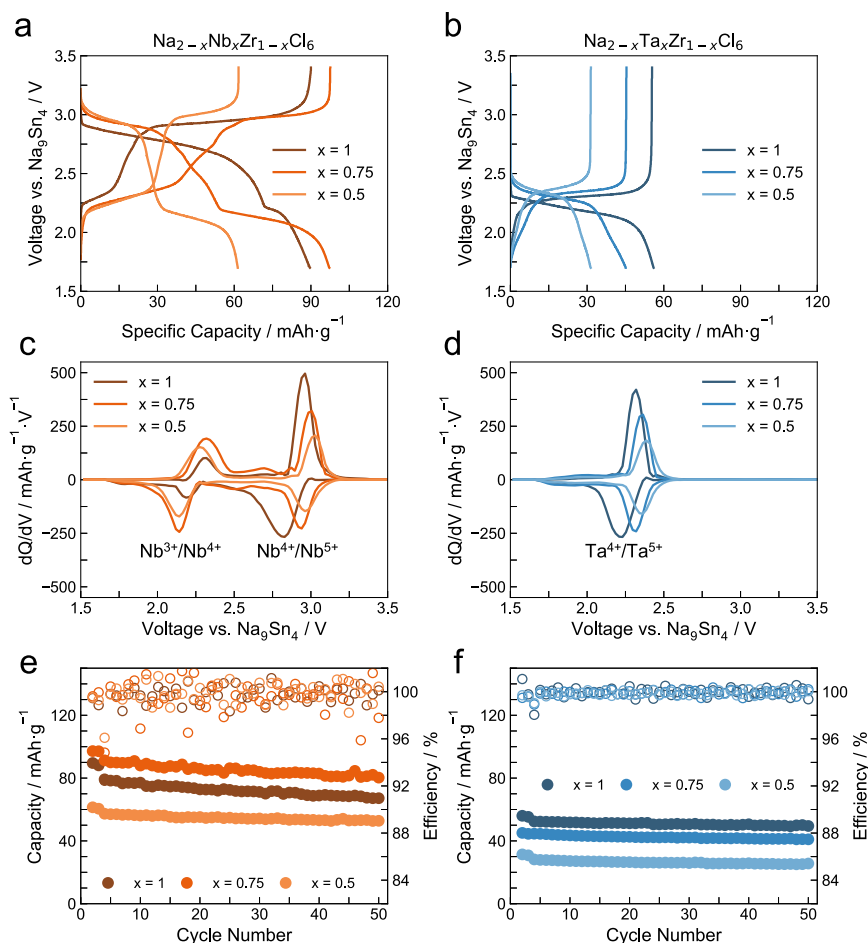
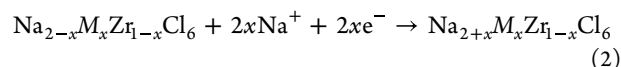
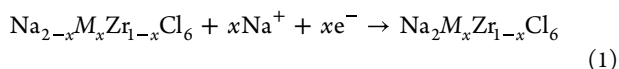


Figure 4. (a, b) First cycle voltage profiles, (c, d) first cycle differential capacity plots, and (e, f) discharge capacity retention plots for Nb-substituted (orange) and (b) Ta-substituted (blue) $\text{Na}_{2-x}\text{M}_x\text{Zr}_{1-x}\text{Cl}_6$ ($M = \text{Nb}$ or Ta) solid solutions, respectively. Solid-state half-cells were cycled by using $\text{Na}_{2-x}\text{M}_x\text{Zr}_{1-x}\text{Cl}_6$ solid electrolytes as the sole active material.

while the vacancy concentration is at its highest in the NaTaCl_6 , the ionic conductivity is slightly lower than for the $x = 0.75$ case, which could be due to a decrease in the number of mobile carriers, or a higher activation energy resulting from restricted transport in the Na^+ vacancy layer.

While the electrochemical properties of niobium^{33–35} and tantalum^{33,36,37} pentoxides have been reported in the literature, no studies, to best of our knowledge, have reported on or discussed the intercalation processes of niobium or tantalum chlorides. Therefore, electrochemical experiments were conducted using various Nb-substituted and Ta-substituted solid-solutions as working electrodes. Solid-state cells were assembled using a $\text{Na}_4(\text{B}_{10}\text{H}_{10})(\text{B}_{12}\text{H}_{12})$ solid electrolyte separator, Na_9Sn_4 counter/reference electrode, and $\text{Na}_{2-x}\text{M}_x\text{Zr}_{1-x}\text{Cl}_6$ ($M = \text{Nb}$ or Ta ; $x = 0.5, 0.75$, or 1) powders mixed with 10 wt % vapor-grown carbon fibers (VGCF) as the working electrode. Due to the irreversible reduction of Zr^{4+} to Zr metal below ~ 1.5 – 1.7 V vs Na_9Sn_4 ¹⁰ the lower voltage limit was set to 1.7 V. Electrochemical sodiation was carried out at a slow $C/10$ (dis)charge rate to minimize any kinetic limitations. The specific capacity was calculated from the following electrochemical reactions for either a one- or two-electron transition-metal redox process:



As expected, NaNbCl_6 and NaTaCl_6 end-members possess the highest specific capacities of 81.6 and 64.3 mAh g^{-1} for a one-electron redox process (intercalation of 1 mol of Na per formula unit), respectively, and 163.2 and 128.6 mAh g^{-1} for a two-electron redox process (intercalation of 2 mol of Na per formula unit), respectively. The calculated specific capacities for all relevant solid-solutions are summarized in [Supplementary Table S8](#). The first cycle voltage profiles for the Nb-substituted and Ta-substituted series are shown in [Figure 4a](#) and [Figure 4b](#), respectively, with formation discharge profiles shown in [Supplementary Figure S8](#). All three Nb-substituted $\text{Na}_{2-x}\text{Nb}_x\text{Zr}_{1-x}\text{Cl}_6$ ($x = 0.5, 0.75$, or 1) solid-solutions exhibit similar voltage profiles, with two distinct close-to-linear sloping regions at ~ 2.85 – 2.9 V and ~ 2.2 V corresponding to $\text{Nb}^{5+}/\text{Nb}^{4+}$ and $\text{Nb}^{4+}/\text{Nb}^{3+}$ redox couples, respectively, which result in high intercalation capacities of 60 – 100 mAh g^{-1} . Interestingly, the Na^+ intercalation voltage for these chloride materials is much higher than what has been reported for Nb_2O_5 , which exhibits an intercalation voltage below 2 V vs Na^+/Na .³⁸ This suggests a stark difference in the nature of the Nb–Cl bond, which possesses a higher energy for niobium reduction as evidenced by its higher electrochemical potential that may be attributed to a larger degree of electron localization and higher valence electron binding energy to

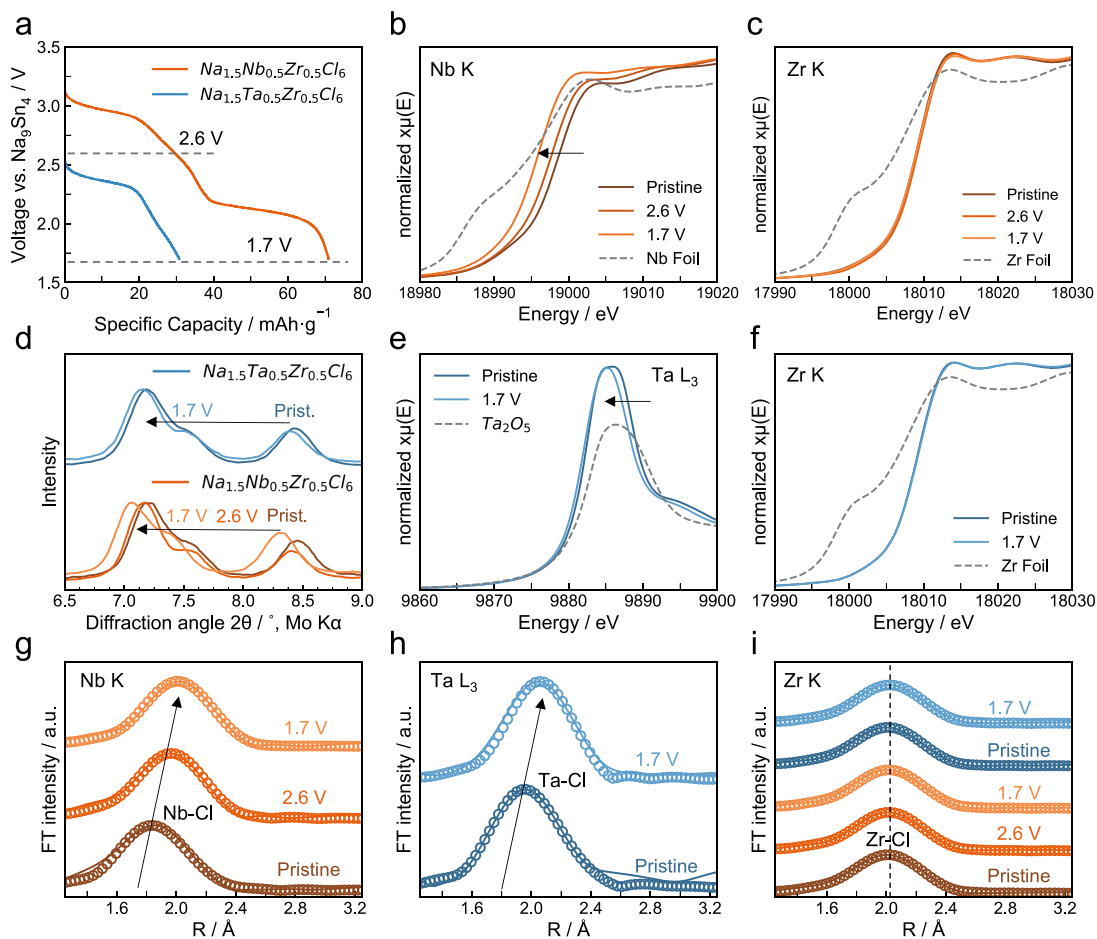


Figure 5. (a) Discharge (sodiation) voltage profiles, Nb K-edge XANES, and Zr K-edge XANES of pristine and sodiated $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ (orange) powders. (c) XRD patterns of sodiated $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ and $\text{Na}_{1.5}\text{Ta}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ powders. (d) Ta L_3 -edge XANES, and Zr K-edge XANES of pristine and sodiated $\text{Na}_{1.5}\text{Ta}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ (blue) powders. (f) K^3 -weighted Fourier transform magnitudes of (g) Nb K-edge, (h) Ta L_3 -edge, and (i) Zr K-edge spectra in pristine and sodiated $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ (orange) and $\text{Na}_{1.5}\text{Ta}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ (blue) powders with first shell fits.

the niobium cation. Although the NaNbCl_6 ($x = 1$) end-member contains the highest concentration of active Nb^{5+} metal centers, and thus the highest theoretical specific capacity, the $\text{Na}_{1.25}\text{Nb}_{0.75}\text{Zr}_{0.25}\text{Cl}_6$ ($x = 0.75$) composition delivers slightly higher capacity in testing due to its higher ionic conductivity and therefore improved Na^+ diffusion kinetics. The NaNbCl_6 ($x = 1$) exhibits a markedly lower ionic conductivity (1 order of magnitude) in comparison to the other Nb-substituted compositions, which leads to a higher cell overpotential that is evidenced in the voltage profile and dQ/dV plots in Figure 4c. Enhanced ionic conductivity of the Nb-substituted solid-solutions generally yields lower overpotentials and therefore higher active material utilization. The Ta-substituted $\text{Na}_{2-x}\text{Ta}_x\text{Zr}_{1-x}\text{Cl}_6$ ($x = 0.5, 0.75, 1$) solid-solutions exhibit a single distinct close-to-linear sloping region in the voltage profile at 2.3 V, corresponding to Na^+ intercalation and the $\text{Ta}^{5+}/\text{Ta}^{4+}$ redox couple. Given that both niobium and tantalum cations show the same valence, coordination, and crystal structure, the lower electrochemical potential of the $\text{Ta}^{5+}/\text{Ta}^{4+}$ redox couple can be attributed to the lower binding energy of tantalum 5d electrons, corresponding to a lower energy of electron transfer.³⁹ The $\text{Ta}^{4+}/\text{Ta}^{3+}$ redox couple which enables a two-electron redox process was not accessible in the solid-solution compositions due to the reduction of Zr^{4+} at lower voltages. However, the $\text{Ta}^{4+}/\text{Ta}^{3+}$ redox couple was confirmed in the NaTaCl_6 end-member (Supplementary

Figure S9). To probe the reversibility of these M^{5+} redox reactions, capacity retention plots are shown in Figure 4e and Figure 4f, for the $\text{Na}_{2-x}\text{Nb}_x\text{Zr}_{1-x}\text{Cl}_6$ ($x = 0.5, 0.75, 1$) and $\text{Na}_{2-x}\text{Ta}_x\text{Zr}_{1-x}\text{Cl}_6$ ($x = 0.5, 0.75, 1$) solid solutions, respectively.

To further confirm the redox activity of Nb^{5+} and Ta^{5+} metal centers and to investigate whether Zr^{4+} metal centers participate in charge storage, X-ray absorption spectroscopy measurements were carried out on Nb-substituted $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ and Ta-substituted $\text{Na}_{1.5}\text{Ta}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ powders in the pristine state and after electrochemical sodiation to various states of charge (2.6 and 1.7 V vs Na_9Sn_4) (Figure 5a). For reference, X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data were also collected on all pristine $\text{Na}_{2-x}\text{M}_x\text{Zr}_{1-x}\text{Cl}_6$ ($M = \text{Nb}$ or Ta ; $0 \leq x \leq 1$) powders (Supplementary Figure S10 and S11). Niobium K-edge (Figure 5b) XANES plots for $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ powders reveal a shift in edge energy from 18998.9 to 18997.9 eV (2.6 V vs Na_9Sn_4) and 18995.8 eV (1.7 V vs Na_9Sn_4), corresponding to discharge capacities of 29.0 mAh g^{-1} (nominal composition: $\text{Na}_{1.9}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$) and 70.9 mAh g^{-1} (nominal composition: $\text{Na}_{2.4}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$), respectively. This indicates a reduction in the niobium oxidation state upon electrochemical sodiation, corresponding to an approximate edge position shift of 2 eV per oxidation state. Zirconium K-edge XANES plots for the same samples reveal no change in

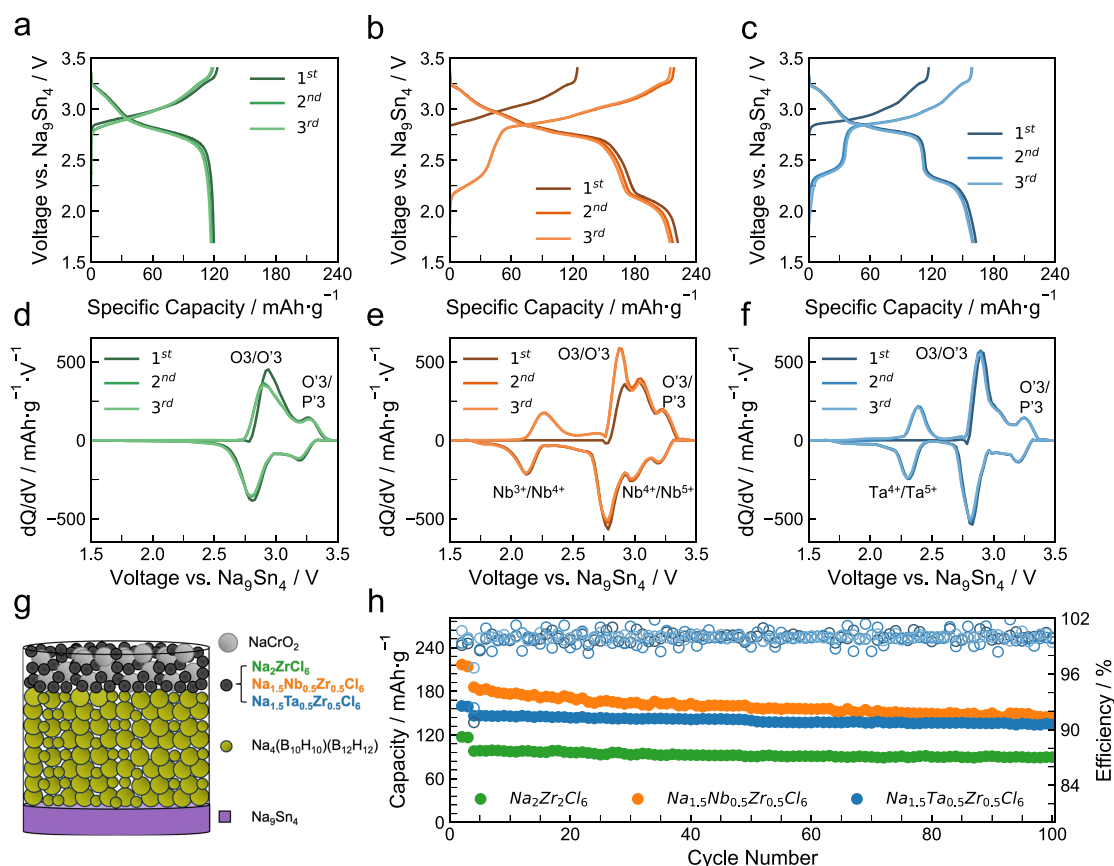


Figure 6. (a, b, c) First cycle voltage profiles and (d, e, f) first cycle differential capacity plots for solid-state half-cells using NaCrO_2 active material paired with Na_2ZrCl_6 , $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$, and $\text{Na}_{1.5}\text{Ta}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ catholytes, respectively. (g) Cell schematic depicting half-cell configuration used for electrochemical testing. (h) Capacity retention plot comparing cell performance with different catholytes. Specific capacities were determined by normalizing (dis)charge capacity by the NaCrO_2 active material mass.

edge position upon sodiation, indicating that zirconium metal centers remain electrochemically inactive and do not participate in Na-ion charge storage reactions directly. X-ray diffraction measurements, shown in Figure 5d, confirm that the monoclinic ($P2_1/n$) structure is maintained during sodiation and exhibits a minor expansion of the unit cell as the structure accommodates additional Na-ions, which is evidenced by a shift of Bragg peaks to lower diffraction angles. XRD patterns, Le Bail fits, and unit cell lattice constants as a function of sodiation degree are given in Supplementary Figures S12, S13, and S14, showing that the monoclinic structure is retained and lattice parameters relax toward their initial values after recharging. Similarly, Ta-substituted $\text{Na}_{1.5}\text{Ta}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ powders were sodiated to a voltage cutoff of 1.7 V vs Na_9Sn_4 corresponding to 30.8 mAh g^{-1} and a nominal composition of $\text{Na}_{1.9}\text{Ta}_{0.5}\text{Zr}_{0.5}\text{Cl}_{0.6}$. Tantalum L_3 -edge XANES plots reveal an edge shift from 9882.6 to 9882.0 eV in edge position for the pristine and reduced states, respectively. Zirconium K-edge XANES shows no shift in edge position upon sodiation, again indicating that Zr metal centers remain electrochemically inactive and suggesting similar charge storage mechanisms occur in both Nb-substituted and Ta-substituted materials.

To provide further evidence for this hypothesis and to investigate the effect of sodiation on the local structure of M–Cl octahedra, Nb K-edge, Ta L_3 -edge, and Zr K-edge EXAFS regions were examined for both Nb and Ta chemistries. K^3 -weighted Fourier transform magnitudes along with first shell fits are shown for Nb K-edge EXAFS (Figure 5g), Ta L_3 -edge

EXAFS (Figure 5h), and Zr K-edge EXAFS (Figure 5i) for Nb-substituted $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ and Ta-substituted $\text{Na}_{1.5}\text{Ta}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ powders. First-shell fitting results, summarized in Supplementary Table S9 and S10, reveal an increase in average Nb–Cl bond length from 2.36 Å in the pristine state to 2.43 and 2.50 Å for sodiated states at 2.6 and 1.7 V, respectively. Initially, NbCl_6 octahedra are distorted in the pristine state and are modeled with two characteristic bond lengths of 2.30 and 2.43 Å, resulting in an average Nb–Cl bond length of 2.37 Å. However, upon sodiation to 2.6 V, the $\text{Nb}^{5+}/\text{Nb}^{4+}$ redox couple is activated and as the Nb^{4+} oxidation state is reached, Nb–Cl octahedra become more symmetric and can be modeled by a single Nb–Cl bond length of 2.43 Å. Furthermore, as the $\text{Nb}^{4+}/\text{Nb}^{3+}$ redox couple is activated upon further sodiation to 1.7 V, Nb–Cl octahedra become distorted, like in the pristine state, but with markedly longer Nb–Cl bond distances of 2.56 and 2.44 Å, giving rise to an average Nb–Cl bond length of 2.50 Å. The increase in Nb–Cl bond length agrees well with the XANES result indicating a decrease in niobium oxidation state as has been commonly reported for oxide systems.⁴⁰ Because Zr–Cl octahedra are electrochemically inactive, as indicated by the zirconium K-edge XANES results, the Zr–Cl bond length does not significantly change with the degree of sodiation. Moreover, the Zr–Cl octahedra are well described by a single bond length of 2.47 Å, indicating a high symmetry of the octahedra. The fact that the bond length and symmetry of Zr–Cl octahedra remain unchanged during sodiation, coupled with the static K-edge position,

provides strong evidence that zirconium remains electrochemically inactive. It is possible that inactive zirconium cations serve to maintain the structural integrity during (de)sodiation by reducing the volumetric change experienced by the crystal, which may explain the improved reversibility of the Zr-containing $\text{Na}_{2-x}\text{Nb}_x\text{Zr}_{1-x}\text{Cl}_6$ compositions compared to the Zr-free NaNbCl_6 end-member. A similar story was observed for sodiated $\text{Na}_{1.5}\text{Ta}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ samples, as Ta^{5+} metal centers are reduced to Ta^{4+} an increase from 2.385 to 2.422 Å in the Ta–Cl bond length was observed, which, again coupled with the shift in Ta L_3 -edge energy, provide strong evidence for the electrochemical activation of the $\text{Ta}^{5+}/\text{Ta}^{4+}$ redox couple. Moreover, negligible changes in the Zr–Cl bond were observed during sodiation, similar to what was found for the Nb-substituted $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ sample.

To investigate how such redox-active solid electrolytes behave with commonly used oxide cathodes, half-cells were assembled using Na_2ZrCl_6 , $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$, $\text{Na}_{1.5}\text{Ta}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$, NaNbCl_6 , or NaTaCl_6 as catholytes and NaCrO_2 as the active cathode material, schematically depicted in Figure 6f. The voltage profiles for the cell assembled using inactive Na_2ZrCl_6 as the catholyte, shown in Figure 6a, exhibited an open-circuit voltage (OCV) of 2.6 V vs Na_9Sn_4 and provided a charge capacity of roughly 120 mAh g^{-1} , similar to previously reported voltage profiles and capacity values for the NaCrO_2 cathode.^{11,41–43} Differential capacity plots, shown in Figure 6d, show two redox reactions at ~ 2.8 and ~ 3.3 V vs Na_9Sn_4 , which correspond to the $\text{Cr}^{3+}/\text{Cr}^{4+}$ redox couple that first undergoes an O3 (rhombohedral) to O'3 (monoclinic) followed by an O'3 (monoclinic) to P'3 (monoclinic) transition.^{41,42} The cell assembled with $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ catholyte exhibited a higher OCV of 2.8 V vs Na_9Sn_4 , but similarly delivered a first charge capacity of 120 mAh g^{-1} . This would indicate that the Nb^{5+} in the catholyte cannot be oxidized further, as expected from this d^0 cation, but this point will be revisited below. On first discharge, however, a specific capacity of approximately 220 mAh g^{-1} was obtained, nearly double the charge capacity of the cell. This is attributed to the activation of the $\text{Nb}^{5+}/\text{Nb}^{4+}$ and $\text{Nb}^{4+}/\text{Nb}^{3+}$ redox couples, which allow for additional Na-ion storage within the $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ structure via intercalation as previously shown when cycled as the standalone active material. Differential capacity plots, shown in Figure 6e, reveal that the expected $\text{Cr}^{4+}/\text{Cr}^{3+}$ redox couple occurs alongside the $\text{Nb}^{5+}/\text{Nb}^{4+}$ and $\text{Nb}^{4+}/\text{Nb}^{3+}$ redox couples. Supplementary Figure S15 shows overlaid differential capacity plots for mixed composites (i.e., NaCrO_2 + catholyte) and catholytes acting as standalone active materials for clarity.

Although the charge capacity of NaCrO_2 is the same with or without $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$, the detailed charge mechanism of the NaCrO_2 – $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ composite is more nuanced than simply assuming that the catholyte is inactive. Close inspection of the first charge differential capacity profile reveals diminished capacity from the NaCrO_2 O3–O'3 transition and the presence of the $\text{Nb}^{5+}/\text{Nb}^{4+}$ redox couple, indicating that chemical oxidation of the NaCrO_2 cathode and reduction of the $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ catholyte occurs during physical mixing when preparing the composite. This effect can be explained by the difference in the OCV between NaCrO_2 (2.5 V) and $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ (2.8 V), which creates a chemical potential gradient and thus a driving force for chemical transfer of Na-ions and electrons between the two materials in the pristine state. X-ray diffraction measurements (Supplementary Figure

S16) prove that this chemical reaction does not negatively impact the crystalline structures of NaCrO_2 and $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ as they remain intact with minor lattice parameter changes corresponding to the sodium transfer. Differential capacity plots for subsequent cycles also demonstrate the reversibility of the NaCrO_2 and $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ redox reactions. Cells were also assembled using $\text{Na}_{1.5}\text{Ta}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ as the catholyte material and NaCrO_2 as the cathode active material and tested as shown in Figure 6c. An OCV of 2.6 V, comparable to the cell using Na_2ZrCl_6 catholyte, was observed and a first charge capacity of 120 mAh g^{-1} was obtained, again indicating typical utilization of the NaCrO_2 cathode sodium storage capacity. During the first discharge, the $\text{Ta}^{5+}/\text{Ta}^{4+}$ redox couple is activated around 2.3 V vs Na_9Sn_4 , below that of the $\text{Cr}^{4+}/\text{Cr}^{3+}$ redox couple. The $\text{Ta}^{4+}/\text{Ta}^{3+}$ redox couple remains inaccessible due to the lower voltage cutoff of 1.7 V vs Na_9Sn_4 . Activation of the $\text{Ta}^{5+}/\text{Ta}^{4+}$ redox couple results in an enhanced discharge capacity of around roughly 165 mAh g^{-1} . In the tantalum case, differential capacity plots shown in Figure 6f, do not show activation of the $\text{Ta}^{5+}/\text{Ta}^{4+}$ redox couple during the first charging cycle, indicating that chemical reduction of $\text{Na}_{1.5}\text{Ta}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ and oxidation of NaCrO_2 do not spontaneously occur during preparation of the cathode composite. This can again be explained by differences in the OCV. In this case, NaCrO_2 possesses a higher OCV than $\text{Na}_{1.5}\text{Ta}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$, resulting in no driving force for the reaction between the two materials. To highlight the improvement in capacity and further demonstrate the reversibility of the variously prepared cathode composites, all cells were cycled for 100 cycles at a C/3 (dis)charging rate, shown in Figure 6h. Generally, cells employing Na_2ZrCl_6 and $\text{Na}_{1.5}\text{Ta}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ catholytes exhibited superior reversibility with capacity retention values of 91% and 92%, respectively, while cells employing $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ catholyte exhibited remarkably high specific capacity with a capacity retention of 79% obtained after 100 cycles. The difference in capacity retention may be attributed to the high storage capacity obtained when employing the $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ catholyte, which is a consequence of the two-electron redox process leveraged, resulting in an activation of both $\text{Nb}^{5+}/\text{Nb}^{4+}$ and $\text{Nb}^{4+}/\text{Nb}^{3+}$ redox couples. As evidenced by the EXAFS and XRD results, significant expansion and contraction of the unit cell, attributed to accommodation of Na-ions and changes in Nb–Cl bond lengths, could result in capacity fade stemming from contact loss between the cathode and catholyte particles. Differential capacity plots (Supplementary Figure S16) reveal capacity loss in both the O3/O'3 reaction of NaCrO_2 and the $\text{Nb}^{5+}/\text{Nb}^{4+}$ redox couple after 50 cycles. The $\text{Nb}^{4+}/\text{Nb}^{3+}$ redox couple shows particularly diminished capacity after 50 cycles, which may partially result from increased overpotential due to higher current density used after the initial 3 cycles and poorer ionic conductivity of the $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ catholyte making this lower voltage redox couple less accessible. However, alternative explanations, such as structural degradation of the $\text{Na}_{1.5}\text{Nb}_{0.5}\text{Zr}_{0.5}\text{Cl}_6$ catholyte when in contact with the cathode, cannot be ruled out entirely.

CONCLUSION

In conclusion, a novel approach leveraging redox-active catholytes to boost the capacity of all-solid-state batteries was proposed and demonstrated. By careful selection of both redox-active and inactive metal centers, combined with an aliovalent substitution strategy, two new series of catholyte

compounds with enhanced ionic conductivities and tunable specific capacities were synthesized. X-ray absorption spectroscopy and electrochemical testing revealed that Nb-containing catholytes undergo reversible two-electron redox at the Nb center, Ta-containing catholytes undergo a reversible single-electron redox process at the Ta center, and Zr sites are redox inactive above 1.7 V and irreversible below 1.7 V vs Na_9Sn_4 . This study reports for the first time on the redox properties of early transition metal chloride compounds and evaluates their use as standalone cathodes and as catholytes when paired with oxide-based cathodes, such as NaCrO_2 . These chloride materials show great promise as active catholyte materials, although additional research is needed to explore other suitable redox-active candidate materials to further improve specific capacities.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.4c14670>.

Additional experimental materials (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Kent J. Griffith – Department of Chemistry and Biochemistry, University of California, San Diego, California 92093, United States; Program of Materials Science and Engineering, University of California San Diego, La Jolla, California 92093, United States; orcid.org/0000-0002-8096-906X; Email: k3griffith@ucsd.edu

Ying Shirley Meng – Department of Nano Engineering, University of California San Diego, La Jolla, California 92093, United States; Pritzker School of Molecular Engineering, The University of Chicago, Chicago, Illinois 60637, United States; orcid.org/0000-0001-8936-8845; Email: shirleymeng@uchicago.edu

Authors

Phillip Ridley – Department of Nano Engineering, University of California San Diego, La Jolla, California 92093, United States

George Duong – Department of Nano Engineering, University of California San Diego, La Jolla, California 92093, United States

Sarah L. Ko – Department of Chemistry and Biochemistry, University of California, San Diego, California 92093, United States

Jin An Sam Oh – Department of Nano Engineering, University of California San Diego, La Jolla, California 92093, United States; orcid.org/0000-0001-9336-234X

Grayson Deysher – Program of Materials Science and Engineering, University of California San Diego, La Jolla, California 92093, United States

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/jacs.4c14670>

Notes

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