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A highly Li^+ -conductive $\text{HfNb}_{24}\text{O}_{62}$ anode material for superior Li^+ storage[†]

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Highly Li^+ -conductive $\text{HfNb}_{24}\text{O}_{62}$ is explored as a new intercalation-type niobium-based oxide anode material for superior Li^+ storage. $\text{HfNb}_{24}\text{O}_{62}$ owns a Wadsley–Roth shear structure with a large unit-cell volume, leading to a large Li^+ diffusion coefficient. $\text{HfNb}_{24}\text{O}_{62}$ shows a large capacity, safe operating potential, high rate performance and good cyclability.

Safe lithium-ion batteries (LIBs) with high power and energy density for electric vehicles (EVs) and hybrid electric vehicles (HEVs) have attracted intense attention.¹ However, the traditional graphite anode material is limited in such applications due to its low kinetics and unsafe lithiation potential.² As a promising substitute for graphite, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is appealing due to its safe operating potential (~ 1.57 V) and high rate performance after proper modifications.³ However, the small theoretical capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (175 mA h g^{-1}) has limited its large-scale applications. Therefore, new anode materials for safe, high-power and high-energy LIBs have been pursued.

In recent years, intercalation-type niobium-based oxides, such as $\text{Ti}_2\text{Nb}_{2x}\text{O}_{4+5x}$ ($x = 2, 5$ and 24),^{4–11} $\text{MNb}_{11}\text{O}_{29}$ ($\text{M} = \text{Al, Cr, Fe}$ and Ga),^{12–15} and $\text{W}_5\text{Nb}_{16}\text{O}_{55}$,¹⁶ have been developed as potential candidates to replace $\text{Li}_4\text{Ti}_5\text{O}_{12}$ due to their comparably safe operating

potentials and much larger theoretical/practical capacities. Niobium is an appealing redox center in electrode materials because of its safe potential window in the range of 1.0–2.0 V for the redox couples of $\text{Nb}^{4+}/\text{Nb}^{5+}$ and $\text{Nb}^{3+}/\text{Nb}^{4+}$, which can avoid the formation of dangerous lithium dendrites.⁴ In light of multivalent properties, niobium-based oxides can deliver large theoretical capacities of 374–416 mA h g^{-1} , which are close to that of graphite and significantly surpass that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. In addition, with reported open Wadsley–Roth shear crystal structures consisting of 96–100% MO_6 octahedra and 0–4% MO_4 tetrahedra,⁴ niobium-based oxides have been identified as typical intercalation-pseudocapacitive materials, which are beneficial for the capacity and fast-charging property. Despite such attractive features, niobium-based oxide anodes still show poor rate performance due to their intrinsically low Li^+ conductivities. Therefore, developing new niobium-based oxide anode materials with high Li^+ conductivities, Li^+ -storage capacities, rate performance, and long-term stability is essential.

In this study, $\text{HfNb}_{24}\text{O}_{62}$ was synthesized by a facile and cost-effective solid-state reaction, and applied as a novel niobium-based oxide anode material with a high Li^+ conductivity to boost the Li^+ storage. In octahedral coordination, the Hf^{4+} ionic radius (0.710 Å) is larger than those of Ti^{4+} (0.605 Å), Al^{3+} (0.535 Å), Cr^{3+} (0.615 Å), Fe^{3+} (0.550 Å), Ga^{3+} (0.620 Å) and W^{6+} (0.600),¹⁷ leading to increased lattice constants and unit-cell volume in $\text{HfNb}_{24}\text{O}_{62}$. A larger unit-cell volume usually corresponds to faster Li^+ diffusivity, benefiting the Li^+ transport kinetics.¹⁸ Moreover, $\text{HfNb}_{24}\text{O}_{62}$ exhibits a monoclinic Wadsley–Roth shear crystal structure (space group of $C2$) consisting of 96% edge-sharing $(\text{Hf},\text{Nb})\text{O}_6$ octahedra linked by 4% $(\text{Hf},\text{Nb})\text{O}_4$ tetrahedra, in which Hf^{4+} and Nb^{5+} are disorder located. This three-dimensional skeleton bestows fast Li^+ diffusivity and high structural stability, guaranteeing fast lithiation/delithiation and excellent cyclability. Both the $\text{HfNb}_{24}\text{O}_{62}/\text{Li}$ half-cell and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{HfNb}_{24}\text{O}_{62}$ full-cell exhibit superior electrochemical properties for fast-charging, large-capacity, safe and durable Li^+ storage.

The detailed crystal structure of the as-prepared $\text{HfNb}_{24}\text{O}_{62}$ material was studied by XRD and a Rietveld refinement of the XRD pattern (Fig. 1a).¹⁹ The characteristic peaks of $\text{HfNb}_{24}\text{O}_{62}$

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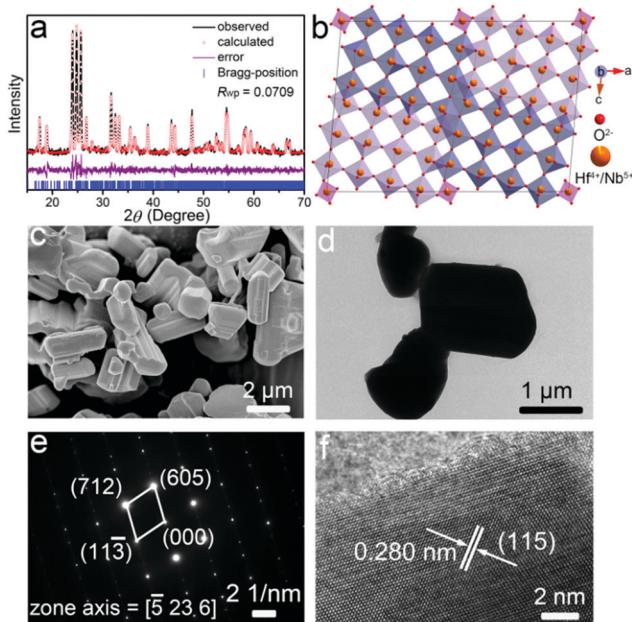


Fig. 1 (a) XRD pattern, (b) crystal structure, (c) FESEM image, (d) TEM image, (e) SAED pattern, and (f) HRTEM image of $\text{HfNb}_{24}\text{O}_{62}$. R_{wp} : weighted profile residual.

are consistent with those of $\text{TiNb}_{24}\text{O}_{62}$ (space group of $C2$).⁶ $\text{HfNb}_{24}\text{O}_{62}$ owns a robust crystal structure, with the structural unit having a 3×4 $(\text{Hf}, \text{Nb})\text{O}_6$ octahedron-block and a half $(\text{Hf}, \text{Nb})\text{O}_4$ tetrahedron at the block corner (Fig. 1b). The lattice parameters were Rietveld-refined to be $a = 29.92508(125)$ Å, $b = 3.82525(14)$ Å, $c = 21.21133(87)$ Å, $\beta = 95.068(5)$ °, and $V = 2418.588(167)$ Å³. Detailed lattice parameters are given in Table S1 (ESI†). Due to the larger Hf^{4+} (0.710 Å) ionic radius than Ti^{4+} (0.605 Å), the unit-cell volume of $\text{HfNb}_{24}\text{O}_{62}$ is larger than that of $\text{TiNb}_{24}\text{O}_{62}$,⁶ which implies wider Li^+ transport pathways in the $\text{HfNb}_{24}\text{O}_{62}$ lattice. The survey XPS spectrum of $\text{HfNb}_{24}\text{O}_{62}$ reveals the presence of Hf, Nb, O and C (reference) elements (Fig. S1a, ESI†). The detailed Hf-4f (Fig. S1b, ESI†) and Nb-3d (Fig. S1c, ESI†) spectra indicate that the Hf and Nb valence states are +4 and +5,^{4,20} respectively.

The FESEM (Fig. 1c) and TEM (Fig. 1d) images reveal that the $\text{HfNb}_{24}\text{O}_{62}$ material is composed of irregular and dense particles with particle sizes varying from ~ 2 to ~ 10 μm, giving a low specific surface area of $0.38 \text{ m}^2 \text{ g}^{-1}$ (Fig. S2, ESI†). The corresponding SAED pattern in Fig. 1e confirms high crystallinity and reveals a single-crystalline feature of the $\text{HfNb}_{24}\text{O}_{62}$ primary particles. An interplanar spacing of 0.280 nm measured from the HRTEM image (Fig. 1f) corresponds to the (115) crystallographic plane of $\text{HfNb}_{24}\text{O}_{62}$. Besides, the EDX mappings (Fig. S3, ESI†) indicate that the Nb, O and Hf elements are well-dispersed in the whole microparticle, verifying the formation of pure $\text{HfNb}_{24}\text{O}_{62}$.

The electrochemical properties of $\text{HfNb}_{24}\text{O}_{62}$ were mainly studied using half-cells. Fig. 2a shows the CV curves of the $\text{HfNb}_{24}\text{O}_{62}/\text{Li}$ cell for the initial four cycles at a sweep rate of 0.2 mV s^{-1} . The difference in the discharge portion of the first CV curve from the subsequent cycles is likely due to the

incomplete Li^+ extraction from the $\text{HfNb}_{24}\text{O}_{62}$ lattice in the first cycle.²¹ After the first cycle, the peak positions and corresponding currents are very stable, suggesting good electrochemical reversibility and cyclability of $\text{HfNb}_{24}\text{O}_{62}$. In the subsequent sweeps, two highly overlapping CV peak pairs located at $\sim 2.0/\sim 2.0$ and $1.77/1.55$ V were assigned to the reversible transformation for the redox couple of $\text{Nb}^{4+}/\text{Nb}^{5+}$. The shoulder peaks located at $1.34/1.14$ V correspond to the redox couple of $\text{Nb}^{3+}/\text{Nb}^{4+}$.¹² Consequently, the estimated $\text{HfNb}_{24}\text{O}_{62}$ mean operating potential (~ 1.66 V) based on the intermediate potential of two intensive peaks at $1.77/1.55$ V is close to those of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (~ 1.57 V),³ TiNb_2O_7 (~ 1.64 V),⁵ $\text{TiNb}_{24}\text{O}_{62}$ (~ 1.66 V)⁶ and $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ (~ 1.70 V).¹¹ Such a reasonably high operating potential of $\text{HfNb}_{24}\text{O}_{62}$ indicates its high safety performance.

Fig. 2b displays the initial three-cycle discharging/charging curves of the $\text{HfNb}_{24}\text{O}_{62}/\text{Li}$ cell recorded at 0.1C . The observed typical potential plateau at ~ 1.66 V in the discharging/charging curves resulted from a double-phase transformation reaction. The sloping regions at 3.0 – 1.67 and 1.65 – 0.8 V were assigned to two different solid–solution reactions.⁸ $\text{HfNb}_{24}\text{O}_{62}$ shows an initial Coulombic efficiency of 93.8% and large reversible capacity of 272 mA h g^{-1} at 0.1C . This practical capacity of $\text{HfNb}_{24}\text{O}_{62}$ is $>100 \text{ mA h g}^{-1}$ larger than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and surpasses the majority of the reported intercalation-type niobium-based oxide anode materials (Fig. 2c).^{3,4,6,9,10,14–16,22,23} The high initial Coulombic efficiency can be due to the fact that little SEI layers formed on the $\text{HfNb}_{24}\text{O}_{62}$ particle surfaces above 0.8 V.

The rate performance of $\text{HfNb}_{24}\text{O}_{62}$ was investigated at various current rates for every ten cycles, as shown in Fig. 2d and e. $\text{HfNb}_{24}\text{O}_{62}$ delivers large reversible capacities of 223, 195, 174, 138 and 105 mA h g^{-1} at 0.5 , 1 , 2 , 5 and 10C , respectively. When the current rate gradually returns from 10C to 0.5C , the capacity is recovered to its original value. When cycled at 1C , $\text{HfNb}_{24}\text{O}_{62}$ shows a small capacity change from 193 to 182 mA h g^{-1} after 100 cycles, giving 94.3% capacity retention (Fig. 2f and Fig. S4, ESI†). When cycled at 10C , $\text{HfNb}_{24}\text{O}_{62}$ shows 87.1% capacity retention even after 500 cycles during the prolonged cycling (Fig. 2g and Fig. S5, ESI†). Such superior cyclability can be due to the stable crystal structure and good Li^+ -transport kinetics of $\text{HfNb}_{24}\text{O}_{62}$.

To interpret the high rate performance of $\text{HfNb}_{24}\text{O}_{62}$, its Li^+ -storage kinetics was analyzed by additional CV experiments recorded at different sweep rates (Fig. 2h). It was found that the cathodic/anodic CV peak current exhibited power law dependence on the sweep rate with an exponent of 0.67/0.74 (Fig. 2i),^{7,24} suggesting that the pseudocapacitive behaviour significantly contributed to the fast charge storage of $\text{HfNb}_{24}\text{O}_{62}$ since it is well known that exponents of 0.5 and 1 indicate diffusion-controlled and pseudocapacitive charge storage, respectively.

A galvanostatic intermittent titration technique (GITT) with a current pulse at 0.1C for 10 min between rest intervals for 20 min was applied to elucidate the Li^+ diffusion coefficient (D_{Li}) of $\text{HfNb}_{24}\text{O}_{62}$ during the initial two cycles. Based on Fick's second law (see ESI†),²⁵ the evolving D_{Li} of $\text{HfNb}_{24}\text{O}_{62}$ at each potential in the discharging (lithiation) and charging (delithiation) processes is determined and plotted in Fig. 2j. The D_{Li} values show

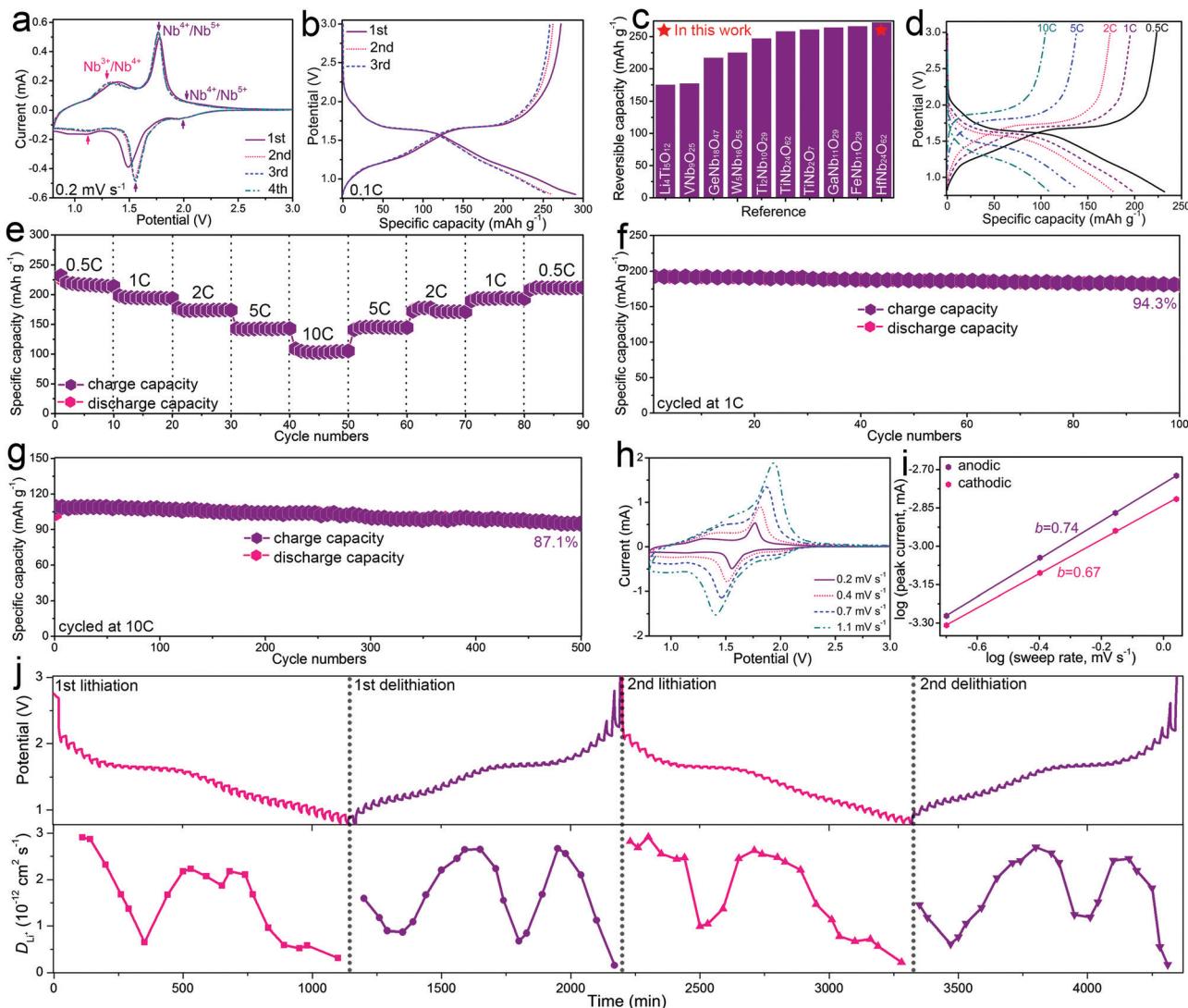


Fig. 2 Electrochemical characterizations of the $\text{HfNb}_{24}\text{O}_{62}/\text{Li}$ cell: (a) CVs at 0.2 mV s^{-1} , (b) discharging/charging curves at 0.1C , (c) comparisons of reversible capacity of $\text{HfNb}_{24}\text{O}_{62}$ with other intercalation-type oxide anode materials, (d) discharging/charging curves at different current rates, (e) rate performance, cyclability at (f) 1C and (g) 10C , (h) CVs at different sweeping rates, (i) exponential relationship between CV peak current and sweep rate, and (j) GITT curves and corresponding Li^+ diffusion coefficients (initial two cycles).

a similar variation trend in the two cycles, and minor values appear in the plateau region ($\sim 1.7 \text{ V}$), where the Li^+ interaction with the host matrix is strong during the two-phase transition reaction. During the first lithiation/delithiation processes, the D_{Li} value varies from 1.51×10^{-13} to $2.91 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, averaging at $1.61 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$. The average D_{Li} value in the second lithiation/delithiation processes ($1.70 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$) is slightly larger than that of the initial cycle, but the curves are similar to those in the initial cycle. It is noteworthy that the Li^+ diffusion coefficient of $\text{HfNb}_{24}\text{O}_{62}$ is significantly larger than those of the reported niobium-based oxide anode materials (Table S2, ESI†), which can be ascribed to its open Wadsley-Roth shear crystal structure with an enlarged unit-cell volume. Clearly, the fast Li^+ diffusivity together with the significant pseudocapacitive behaviour of $\text{HfNb}_{24}\text{O}_{62}$ greatly contributes to its superior Li^+ storage (especially its rate performance).

To demonstrate the practical application of $\text{HfNb}_{24}\text{O}_{62}$, a full cell with a $\text{HfNb}_{24}\text{O}_{62}$ anode and a $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode was fabricated (Fig. 3a). The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{HfNb}_{24}\text{O}_{62}$ full cell affords a large charge capacity of 213 mA h g^{-1} with an average operating voltage of $\sim 3.0 \text{ V}$ at 0.1C (Fig. 3b). This high voltage agrees with the CV result (Fig. 3c). As the current rate gradually increases to $0.5, 1, 2, 5$ and even 10C , the reversible capacity retains $143, 130, 116, 95$ and 78 mA h g^{-1} , respectively (Fig. 3d). When the current rate returns from 10C to 0.5C , the obtained capacity of 141 mA h g^{-1} indicates good electrochemical reversibility (Fig. 3e). The full cell also presents outstanding cyclability at both 1C (83.4% capacity retention after 100 cycles, Fig. 3f) and 5C (84.7% capacity retention after 500 cycles, Fig. 3g). The full cell can power a green light-emitting diode (LED) after being cycled 500 times at 5C (Fig. 3g inset).

In summary, highly- Li^+ -conductive $\text{HfNb}_{24}\text{O}_{62}$ is demonstrated as a novel anode material to realize superior Li^+ storage.

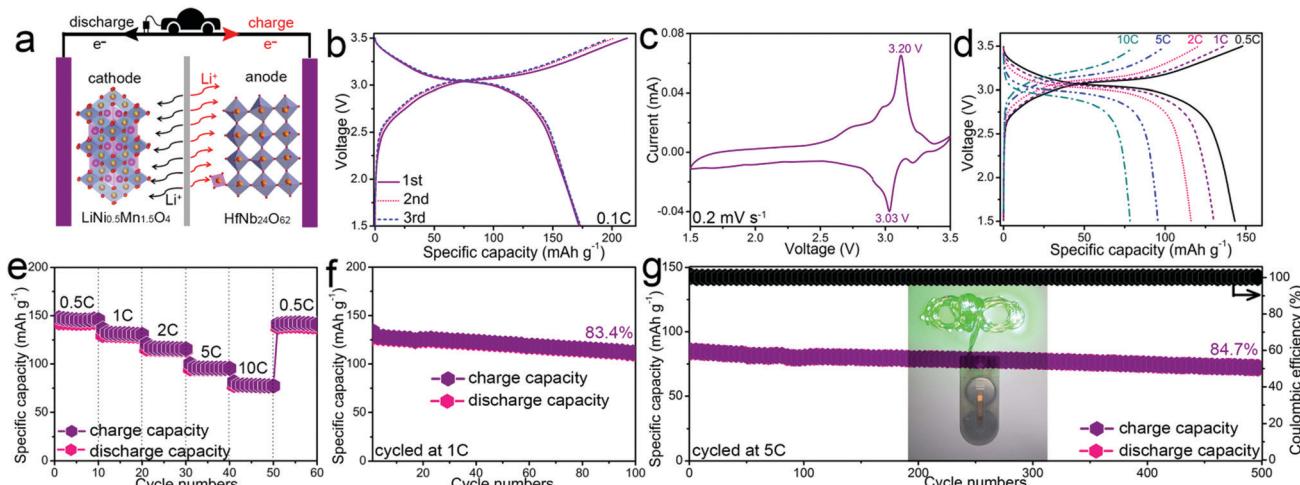


Fig. 3 (a) Schematic illustration of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ // $\text{HfNb}_{24}\text{O}_{62}$ full cell. Electrochemical characterizations of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ // $\text{HfNb}_{24}\text{O}_{62}$ full cell: (b) initial three-cycle charging/discharging curves at 0.1C , (c) CV at 0.2 mV s^{-1} , (d) charging/discharging curves at different current rates, (e) rate performance, and cyclability at (f) 1C and (g) 5C (inset: green LED lit up by the full cell).

Both the open Wadsley–Roth shear crystal structure and enlarged unit-cell volume lead to favorable Li^+ conduction. Benefiting from the robust host framework and fast ion diffusion pathways, $\text{HfNb}_{24}\text{O}_{62}$ exhibits prominent electrochemical properties. At 0.1C , it displays a large capacity of 272 mA h g^{-1} with a relatively safe operating potential of $\sim 1.66\text{ V}$ and a high initial Coulombic efficiency of 93.8% . Even at 10C , a remarkable reversible capacity of 105 mA h g^{-1} is preserved. Furthermore, it exhibits good long-term cyclability, as indicated by 87.1% capacity retention after 500 cycles at 10C . More importantly, a $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ // $\text{HfNb}_{24}\text{O}_{62}$ full cell also exhibits high rate performance with 213 mA h g^{-1} at 0.1C and 78 mA h g^{-1} at 10C , and good long-term cyclability with 84.7% capacity retention after 500 cycles at 5C . This work can benefit the future designs of highly- Li^+ -conductive and fast-charging electrode materials.

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Conflicts of interest

There are no conflicts to declare.

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