Nickel Niobate Anodes for High Rate Lithium-Ion Batteries

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Fast charging is one of the key requirements for next-generation lithium-ion batteries, however, lithium-ion diffusion rates of typical electrode materials are limited. Nanosizing of active electrode material is a common strategy to increase the effective lithium-ion diffusion transport rate, but it also decreases the volumetric energy/power density and stability of the battery. In this work, nickel niobate NiNb$_2$O$_6$ is demonstrated for the first time as a new intrinsic high-rate anode material for lithium-ion batteries without the requirement of realizing nano-architectures. The NiNb$_2$O$_6$ host crystal structure exhibits only a single type of channel for lithium-ion intercalation and can be fully lithiated with a capacity of about 244 mAh g$^{-1}$ at low current densities. Interestingly, a high diffusion coefficient of $10^{-12}$ cm$^2$ s$^{-1}$ at 300 K enables fast (dis)charging at high current densities resulting in high capacities of 140 and 50 mAh g$^{-1}$ for 10 and 100C respectively. The minimal volume change during lithiation is the origin of the stable reversible lithiation process in NiNb$_2$O$_6$ and leads to 81% capacity retention after 20,000 cycles at 100C. Finally, full cell systems against LiFePO$_4$ and Li[Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$]O$_2$ (NCM811) cathodes demonstrate the promising energy storage performance of nickel niobate anodes in practical battery devices.

1. Introduction

Nowadays, fast charging ability of energy storage devices is essential for applications in electric vehicles and electrical power grids. The fast charging performance of batteries is enabled by high-rate electrode materials, which have been realized through various methods such as nanosizing, porous structures, carbon-coatings, and conductive materials-based hierarchical structures. Nanosizing and porous structures can enhance the lithium-ion transport as they reduce the distance lithium ions have to diffuse in the solid electrode, and they also enlarge the contact area between the liquid electrolyte and the electrode material. Carbon-coatings and conductive materials (e.g., graphene or Mxene) based hierarchical structures can enhance the electrical conductivity of the electrodes to enable higher current densities. However, nanosizing and porous structures lead to a reduction of the specific volumetric capacity, while composites with carbon-based conductive materials require the electrode to discharge down to 0.01 V resulting in lithium dendrite formation under high current densities. The formation of nanostructures can even result in a reduced electrochemical performance at high C rates as compared to their bulk materials due to possible morphology change, nano-structure collapse, and higher first-cycle capacity loss. Furthermore, the fabrication of these delicate nano-architectures, porous structures, and composites usually require harsh synthesis environments, expensive reactants, and multiple synthesis steps, which results in a complex and expensive synthesis process. Additionally, such synthesis methods often provide either relatively low yields or significant amounts of chemical waste.

Recent studies increasingly focus on the development of electrode materials with an intrinsic high-rate performance by combining the advantages of exhibiting 1) a suitable host structure for fast lithium-ion intercalation, 2) a lower bandgap to enhance the electrical conductivity, and 3) a higher working voltage to avoid lithium dendrite formation. Titanium-based oxides, such as Li$_4$Ti$_5$O$_12$ and anatase TiO$_2$, are well known as interesting electrode materials, while they exhibit working voltages of 1.55 and 1.8 V respectively, preventing lithium plating. However, in order to obtain high rate performance,
nanosizing is still required for these titanium-based oxides. For example, mesoporous yolk-shell anatase TiO₂/TiO₂(B) microspheres reach capacities of 181 mAh g⁻¹ at a rate of 40 C,[14] while hollow multi-shelled heterostructured anatase TiO₂/TiO₂(B) provide capacities of 125 mAh g⁻¹ at a rate of 20 C.[15] Furthermore, the band gaps of Li₂Ti₅O₁₂ and anatase TiO₂ are 3.14 and 3.2 eV, respectively, which still limits the intrinsic electrical conductivity of these electrode materials.

Also, niobium-based oxides, such as T-phase Nb₂O₅ and niobium tungsten oxides, have attracted attention because of their high rate performance. Porous T-Nb₂O₅ nanoflowers can provide 130 mAh g⁻¹ specific capacity at 5 A g⁻¹ due to its high ionic diffusivity,[16] while the specific capacity of T-Nb₂O₅ nanocrystals can reach 40 mAh g⁻¹ at 1000 C[17] as enabled by its lithium-ion intercalation pseudo-capacitance. More recently, niobium tungsten oxides have shown high rate capabilities caused by its suitable host structure for lithium-ion diffusion. For example, Nb₁₄W₃O₄₄[16] and Nb₁₈W₁₆O₉₃[19] bulk particles reach 57 and 70 mAh g⁻¹ at 100 C, respectively. Unfortunately, the niobium tungsten oxide structure contains multiple types of channels, which results in multiple voltage plateaus and is, therefore, inconvenient for practical usage. Furthermore, the achieved specific capacity at high C rates is still relatively low when taking into account the required capacities for practical high-rate storage devices. Interestingly, nanosizing of these niobium tungsten oxides into nanowires enhances its rate performance and cycling stability, as Nb₁₄W₃O₄₄[16] and Nb₁₈W₁₆O₉₃[19] and Nb₄W₄O₁₂[20] nanowires exhibited specific capacities of 130 (6.7 C), 153 (6.7 C), and 113 mAh g⁻¹ (5 C), respectively. However, ideal high-rate electrode materials should intrinsically exhibit fast lithium-ion diffusion with a single voltage plateau without complex synthesis procedures to minimize the length scales for lithium diffusion in nano-architectures.

In this work, we demonstrate nickel niobate, NiNb₂O₆, as a new electrode material, which exhibits an intrinsic high rate performance enabled by its suitable host crystal structure, as shown in Figure 1, and its large pseudo-capacitance. The NiNb₂O₆ columbite structure contains a single type of channel for lithium-ion intercalation, which leads to a single voltage plateau at 1.6–1.7 V during charge-discharge cycling, facilitating use in practical high-rate lithium-ion batteries. The oxidation of all three transition metal ions enables the structure to fully lithiate up to LiₓNiNb₂O₆ with a capacity of about 244 mAh g⁻¹ at 0.5C. Faster (dis)charging at 1, 5, 10, and 100 C resulted in high capacities of respectively 220, 165, 140, and 50 mAh g⁻¹. The stability of the reversible lithiation process in NiNb₂O₆ is demonstrated by achieving a capacity retention of 81% after 20000 cycles at 100C. The structural stability and electrochemical behavior, with a high diffusion coefficient of 10⁻¹² cm² s⁻¹, were investigated by various experimental techniques and confirmed by density functional theory (DFT) calculations. Finally, full cell systems against LiFePO₄ and NCM811 cathodes demonstrated the promising energy storage performance of NiNb₂O₆ anodes in practical battery devices.

2. Results and Discussion

2.1. Structural Characterization

Nickel niobate, NiNb₂O₆, typically forms a columbite phase (Pbcn)[21,22] exhibiting an orthorhombic crystal structure with lattice parameters of 14.022, 5.675, and 5.015 Å (JCPDS card: No. 01-072-0481), as schematically depicted in Figure 1. In this orthorhombic structure the oxygen atoms form corner-shared octahedra around the Ni²⁺ and Nb⁵⁺ ions, creating isolated zig-zag chains of Ni ions. As there are four formula units per crystallographic unit cell, the structure consists of layers of NiO octahedra at x = 0 and x = 0.5 which are separated by two intervening NbO₆ layers. However, previous studies have also demonstrated the formation of disordered rutile (P4₂/mmm)[23] and tetragonal (P4_j/n)[24] polymorphs. X-ray diffraction (XRD) analysis of our synthesized particles confirmed the formation of the orthorhombic NiNb₂O₆ structure, as shown in Figure 2a.

The morphology and size of the synthesized NiNb₂O₆ particles were investigated by scanning electron microscopy (SEM). The agglomerated particle size is in the range 1–5 μm (Figure S1a, Supporting Information), while the single primary particle size is mainly between 0.3 and 0.8 μm (Figure 1b). The agglomerated particles are formed by stacking of the irregular polyhedron-shaped

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**Figure 1.** a,b) Schematic diagrams of the NiNb₂O₆ host structure.
primary particles. The layered structure of the NiNb₂O₆ phase can be observed in Figure S1b, Supporting Information, which confirms the successful formation of the orthorhombic structure exhibiting a layered structure along the a-axis. Furthermore, the average size of the particles was determined by Brunauer–Emmett–Teller method (BET) analysis in which nitrogen adsorption at different pressures enables determination of the specific surface area of the NiNb₂O₆ powder (1.554 ± 0.003 m² g⁻¹), see Figure S2, Supporting Information. Using a spherical model to express the NiNb₂O₆ powder, the average diameter of the particles was calculated to be 680 ± 1 nm (Table S1, Supporting Information), which matches very well with the observations by SEM analysis. The composition of the NiNb₂O₆ powder was investigated by X-ray fluorescence spectroscopy (XRF) analysis, which confirmed the exact 1:2 atomic ratio between Ni and Nb (Table S2, Supporting Information), which agrees well with the NiNb₂O₆ phase measured by XRD (Figure 2a). X-ray photoelectron spectroscopy (XPS) analysis of the as-prepared NiNb₂O₆ powder shows the Ni 2p½ peak at 856.7 eV and the Nb 3d½ peak at 207.1 eV (Figure 2c,d), which confirms the expected Ni²⁺ and Nb⁵⁺ oxidation states.²⁵,²⁶ Furthermore, XPS analysis was performed on cycled NiNb₂O₆ electrodes at 1.7 and 1.0 V discharged states, as shown in Figure S3, Supporting Information. In comparison to the valence state of niobium in pristine NiNb₂O₆ (Figure 2d), Nb⁵⁺ is gradually reduced to Nb⁴⁺ during the discharge process down to 1.0 V (Figure S3c, Supporting Information), while both Nb⁵⁺ and Nb⁴⁺ are present halfway the discharge process at 1.7 V (Figure S3a, Supporting Information). At the same time the Ni²⁺ peak shifts to a lower binding energy, while Ni⁰ is also present in the NiNb₂O₆ samples discharged to 1.7 and 1.0 V (Figure S3b,S3d, Supporting Information). Although the multiple peak profile of Ni²⁺ warrants further investigation, we may conclude that both Ni and Nb contribute to the redox reactions for lithium storage.

To determine the variations in the NiNb₂O₆ unit cell lattice during lithiation, operando XRD analysis was performed while cycling a mixed NiNb₂O₆ electrode in a half cell against lithium metal at C/8 within the 1.0 to 3.0 V range (Figure 3a). It can be observed that the NiNb₂O₆ (311) diffraction peak shifts following the charge-discharge process (Figure 3b). By using Gaussian fitting, the peak position was determined (Figure 3c), which indicates a reversible shift by 0.03 degrees between the charged and discharged states. These results suggest that the lithium intercalation only causes 0.112% widening between the (311) Miller planes. This minimal change suggests that the crystal structure of nickel niobate is quite stable during the charge-discharge process, which is ideal for fast lithium diffusion.

Figure 2. Structural characterization of the pristine NiNb₂O₆ powder by a) X-ray Diffraction, b) SEM analysis, and c,d) XPS spectra of 2p nickel and 3d niobium levels, respectively.
The observed structural changes in the \( \text{NiNb}_2\text{O}_6 \) crystal structure during lithium intercalation were studied in detail by ex situ scanning transmission electron microscopy (STEM) analysis after cycling of the mixed electrode material in a half cell against lithium metal (Figure 4). Specimens were obtained through focused ion beam along different crystal directions for electrode materials at different voltage states (3, 1.7, and 1 V, representing \( \text{NiNb}_2\text{O}_6 \), \( \text{Li}_{1.5}\text{NiNb}_2\text{O}_6 \), and \( \text{Li}_3\text{NiNb}_2\text{O}_6 \) respectively) from the \( \text{NiNb}_2\text{O}_6 \) host structure until the fully lithiated \( \text{Li}_3\text{NiNb}_2\text{O}_6 \) structure. The STEM images in Figure 4a–c show projections along the (013) Miller plane for the 3 V specimen, along the (311) plane for the 1.7 V specimen, and along the (100) plane for the 1 V specimen. The corresponding strain mappings in Figure 4d–f indicate that the strain inside the crystal lattice is always located in between the layers containing the transition metal ions (Ni and Nb).
This means that the lattice strain is strictly trapped in between the transition metal ion layers and doesn’t develop upon lithium-ion intercalation, resulting in a very stable crystal structure with minimal volume expansion, in good agreement with experimental XRD results. Furthermore, Figure S4a–c, Supporting Information, shows that grain boundaries can be found in the pristine and cycled NiNb₂O₆ powders, which may contribute to the lithium-ion diffusion in NiNb₂O₆ electrodes.

2.2. Theoretical Modeling

To find the most favorable site for a single Li-ion in NiNb₂O₆ (modeled by a 1 × 1 × 2 unit cell: LiₙNiₓNb₉O₂₈), we considered all possible configurations with 1 Li⁺ in 34 possible interstitial sites (with a minimum distance of 1.6–2.0 Å with respect to nearest neighbors) as well as 1 Ni³⁺ and 7 Ni²⁺ in 8 Ni sites, namely, 34! / (33! · 1!) = 272 structures. Total Coulomb energies Eᵣ of 272 structures were calculated using elementary charges of 1 for Li, 5+ for Nb, and 2- for O. By performing density function theory perturbed-burke-ernzerhof (DFT-PBE) calculations on 10 distinguishable topmost electrostatically favorable structures it was found that the lowest total energy structure is the one with the lowest Eᵣ, and that Li prefers occupying octahedral sites. Our ab initio molecular dynamics (AIMD) simulation showed that the most favorable pathway for Li-ion migration is along the c direction. Subsequently, DFT nudged elastic band (DFT-NEB) calculations were used to compute the diffusion barrier ΔE along the c direction (Figure S5, Supporting Information) to be 0.46 eV. Our computed E₀ value is similar to the previously calculated (using DFT or MD) energy barrier of the rate-limiting step for the diffusion of Li in the anatase phase of TiO₂ (E₀ = 0.496 eV).[27] TT-Nb₂O₅ (E₀ = 0.46 eV)[28] and T-Nb₂O₅ (E₀ = 0.47 eV)[28] considering a low Li concentration.

Using the transition state theory, the diffusion coefficient was then computed by

\[ D = \frac{w}{2d} v^2 \exp \left( \frac{E_b}{k_B T} \right) \]  

(1)

where \( w \) and \( d \) are the number of nearest neighbor sites for Li hopping and dimensionality of diffusion, which are 2 and 1, respectively, for NiNb₂O₆. \( v \) is the frequency of a successful jump between successive Li sites (i.e., jump frequency) and was calculated using the harmonic transition state theory approximation

\[ v = \prod_{i}^{N} v_i^c \prod_{i}^{N-1} v_i^{v_i} \]  

(2)

Here, \( v_i^c \) and \( v_i^v \) are the real vibrational frequencies (computed by DFT-PBE calculations) of the ground and transition state, respectively. With a distance of 2.14 Å between two adjacent Li sites (\( L \)) and \( \nu = 1.36 \times 10^{13} \) Hz the diffusion coefficient \( D \) was calculated to be 1.16 \times 10^{-10} \text{cm}^2 \text{s}^{-1} for bulk \( \text{Li}_0.325\text{NiNb}_2\text{O}_6 \) at room temperature (300 K). Our computed diffusion coefficient for this system is higher than the previously calculated value of 5.25 \times 10^{-12} \text{cm}^2 \text{s}^{-1} for diffusion of Li in TiO₂-anatase with a low Li concentration at 300 K.[27]

2.3. Electrochemical Characterization

Electrochemical measurements were performed to determine the performance of NiNb₂O₆ as electrode material for fast charging, high-capacity lithium-ion batteries. Galvanostatic charge-discharge cycling was used to investigate the cycle life of NiNb₂O₆ mixed electrodes (8:1:1 mass ratio). The average voltage of the charge and discharge plateaus is about 1.6 V when cycling at a rate of 1 C, which increases gradually for higher rates of 5C and 10C to respectively 1.65 and 1.72 V (Figure S6, Supporting Information). The initial capacities of these NiNb₂O₆ mixed electrodes at 1, 10, and 100 C are 231, 126, and 60 mAh g⁻¹, respectively, as shown in Figure 5a–c. Interestingly, the specific capacity of NiNb₂O₆ at 1 C is 92.8% of its theoretical capacity, which indicates that the NiNb₂O₆ host structure can be almost fully lithiated up to Li₄NiNb₂O₆. This suggests the oxidation of all three transition metal ions in the NiNb₂O₆ structure within the used voltage range between 1.0 and 3.0 V.

The cycle life performance was investigated for different rates of 1, 10, and 100 C (23.6 A g⁻¹) for 300, 2500, and 20000 cycles, respectively (Figure 5a–c), showing good capacity retention of 97%, 92%, and 81%, respectively. Furthermore, the Coulombic efficiencies in all measurements were stable with values between 99.8% and 100.2%. This high cycling stability demonstrates the stable, reversible lithiation process in NiNb₂O₆ up to very high current densities, and confirms that NiNb₂O₆ is a promising candidate material for high rate electrodes in lithium-ion batteries.

More detailed rate performance measurements were performed on a mixed NiNb₂O₆ electrode (7.5:1.5:1 mass ratio) in a half cell against lithium metal for various current densities between 0.5 and 100 C (Figure 5d). The overall rate performance results show that the NiNb₂O₆ electrode can cycle very stable from a low current density (244 mAh g⁻¹ for 0.5 C) up to a high current density (100 C), and subsequently back to 1 C resulting in a specific capacity (219.8 mAh g⁻¹ after 150 cycles) which is very similar to the initial specific capacity at 1 C (219.2 mAh g⁻¹ after the first 20 cycles). In comparison to the capacity at 0.5C the capacity retentions at higher C rates (1, 2, 5, 10, 20, 50, and 100 C) are respectively 220, 200, 165, 140, 117, 82, and 50 mAh g⁻¹ (e.g., 90.1%, 81.6%, 67.6%, 57.4%, 47.8%, 33.6%, and 20.1%, respectively). Furthermore, the charge-discharge curves show clear voltage plateaus, which are increasing in voltage for higher current densities (Figure 5e). This indicates that the observed capacity decrease for higher current densities originates from an increasing polarization (concentration polarization and electrochemical polarization) creating an enhanced overpotential. It confirms that the NiNb₂O₆ crystal structure remains stable even after charge-discharge cycling at very high current densities, in good agreement with results from our XRD and STEM analysis.

In order to investigate the influence of the electrode resistance to the rate performance of NiNb₂O₆ electrode material, a mixed NiNb₂O₆ electrode (8:1:1 mass ratio) with a slightly lower carbon black contribution was studied as well (Figure S7, Supporting Information). It showed a similar rate performance as compared to the 7.5:1.5:1 mass ratio NiNb₂O₆ electrode (Figure 5) for rates below 20 C. However, for rates of 50 and 100 C, the 7.5:1.5:1 mass ratio NiNb₂O₆ electrode provided a
higher capacity retention than the 8:1:1 mass ratio electrode. This means that a decrease of the resistance by adding 5% more conductive carbon will only show a significant effect for ultrafast charging above 20 C.

The advantage of an intrinsic high-rate electrode material, as compared to nano-sized electrode materials, is most pronounced in the volumetric energy and power densities. Nano-sizing of electrode materials requires an increase in the amount of conductive carbon to provide an optimal conductive network, which has a minimal effect on the weight (i.e., gravimetric densities) but a large effect on the volume, and therefore, the volumetric densities. To compare our results for NiNb2O6 electrodes with previously reported high-rate anode materials a volumetric Ragone plot is shown in Figure 5f. It can be seen that NiNb2O6 exhibits higher energy densities for the full power density range outperforming all other reported materials, and only in the middle power density region, the energy density of NiNb2O6 is similar to Nb18W16O93.[17]

To obtain more in-depth knowledge on lithium-ion intercalation in NiNb2O6, the electrochemical diffusion coefficient of lithium ions in the NiNb2O6 structure was experimentally determined by three different methods: different sweep rate Cyclic Voltammetry (CV), Galvanostatic Intermittent Titration Technique (GITT), and Electrochemical Impedance Spectroscopy (EIS). For the CV measurements four different sweep rates (0.1, 0.2, 0.5, and 1 mV s\(^{-1}\)) were used leading to a dominant reaction peak around 1.7 V during charge and discharge (Figure 6a), in good agreement with the voltage plateaus in Figure 5e. At around 1.1 V, a small peak can be observed which suggests that after Nb\(^{5+}\) to Nb\(^{4+}\) reduction, a small amount of Nb\(^{4+}\) is further reduced to Nb\(^{3+}\), although this was not observed during XPS analysis for the sample at the 1 V discharged state. The linear fit of the peak currents during lithiation and delithiation versus the square root sweep rate is shown in Figure 6b from which lithium-ion diffusion coefficients of \(1.20 \times 10^{-12}\) (lithiation) and \(1.36 \times 10^{-12}\) cm\(^2\) s\(^{-1}\) (delithiation) can be calculated[35] (Figure S8, Supporting Information). Furthermore, following Dunn’s model[36] the \(b\)-value above 0.75 can be determined outside the peak voltage region close to 1.7 V (Figure 6c). This \(b\)-value is an indication of the storage mechanism, and suggests that this NiNb2O6-based battery is a hybrid device and its capacity originates from intercalation and as well as from pseudo-capacitance.

The pseudocapacitive contribution to the storage capacity was investigated in more detail to determine its importance for the lithium storage ability of NiNb2O6 electrodes. The calculation result for 0.5 mV s\(^{-1}\) sweep rate using Dunn’s model[36] shows a high pseudocapacitive contribution (Figure 6d), which explains the excellent rate performance. The pseudocapacitive contribution ratio is increasing with increasing sweep rates up to 82.3% at 1 mV s\(^{-1}\) (Figure 6e), which is similar to nanosized niobates.[17] However, the NiNb2O6 material under investigation
here still remains a bulk powder with particle sizes of about 680 nm (Table S1, Supporting Information). This shows that the host structure of NiNb$_2$O$_6$ crystal is suitable for lithium-ion intercalation, which indicates that this intercalation charge storage process is not limited by lithium-ion diffusion but by the surface process. Thus, the overall capacitive behavior of NiNb$_2$O$_6$ can be explained by its lithium-ion intercalation pseudocapacitive property. The results of the GITT measurements yield calculated lithiation diffusion coefficients of about 1–2 x 10$^{-12}$ cm$^2$ s$^{-1}$ (Figure 6f) during the charge-discharge process, in good agreement with the values calculated from the different sweep rate CV.

EIS measurements were also performed for mixed NiNb$_2$O$_6$ electrodes in the charged and discharged state, and fitted to equivalent circuit models to determine the different contributions. For the discharged state (Figure 7a) the circuit contains a bulk resistance ($R_b$), a separator component, and a charge transfer component.$^{[39]}$ The fit suggests that the resistance of the Li$_x$NiNb$_2$O$_6$ electrode is about 9.9 ± 0.24 Ω cm$^{-2}$. For the charged state (Figure 7b) the EIS measurement is fitted with a different circuit containing a bulk resistance, a separator component, and two charge transfer components, which suggests the existence of a solid-liquid charge transfer at the solid-electrolyte interface as well as a solid-solid charge transfer in
between the NiNb2O6 bulk particles. The results suggest that the resistance of the NiNb2O6 electrode is 7.6 ± 0.34 Ω. This means that the variation in resistance between the charged NiNb2O6 phase and the discharged Li1.5NiNb2O6 phase is very minimal, which is ideal for fast charging electrode materials.

The lithium-ion diffusion coefficients were calculated from the Warburg part of the EIS spectra, as described in detail in the supporting information. We used the method proposed by Ho et al.,[40] in which the slopes of Z’ versus ω−1.5 curves are obtained by linear fits (Figure S10, Supporting Information) and the slopes of the potential versus the numbers of lithium-ions inside the NiNb2O6 structure are obtained by the deviation of the potential versus numbers of lithium-ion curves (Figure S11, Supporting Information). The lithium-ion diffusion coefficients calculated from the EIS spectra are 3.96 × 10−12 cm2 s−1 for the discharged state and 1.21 × 10−12 cm2 s−1 for the charged state. This confirms that the electrochemical lithium-ion diffusion coefficient of the NiNb2O6 electrode is in the 10−12 cm2 s−1 range, in close agreement with the CV and GITT results. To demonstrate the unique high lithium-ion diffusion coefficient in our NiNb2O6 material, a comparison with other high rate anode materials is shown in Table S3, Supporting Information. Fast charging bulk materials, such as titanium- and niobium-based oxides, typically exhibit one or two orders of magnitude lower lithium-ion diffusion coefficients (10−13–10−14 cm2 s−1).[18–20,35,41–44] while only nanosizing Nb5W10O37 down to 50 nm wide nanowires has yielded similar values of about 10−12 cm2 s−1.[29]

2.4. Practical Battery Performance

In order to investigate the electrochemical behavior of NiNb2O6 electrodes under practical conditions, several experiments were performed on thick NiNb2O6 electrodes with practical loading (about 8.5 mg cm−2, 2 mAh cm−2) including half-cell measurements, full cell measurements against commercial cathode materials, and finally experiments with a lean electrolyte contribution. The rate performance of a high loading (~8.5 mg cm−2) NiNb2O6 electrode in a half cell against lithium metal shows similar capacity retention behavior (specific capacity at 20 C is around 50% of the capacity at 1 C, Figure S12a, Supporting Information) as compared to the commonly used low loading (1–3 mg cm−2) for electrochemical performance analysis of high rate electrode materials in other scientific studies. Although the capacity retention for high loading NiNb2O6 electrodes is reduced for high rates above 20 C (Figure S12a, Supporting Information) as compared to low loading NiNb2O6 electrodes (Figure 5d) due to increased internal resistance, they can still deliver 90 mAh g−1 (0.77 mAh cm−2) in a charge-discharge process of only 70 s. The charge-discharge profiles of such high loading NiNb2O6 electrode (Figure S12b, Supporting Information) for different rates show that the voltage bias between the charge and discharge plateaus is larger than the for the low loading NiNb2O6 electrode (Figure 5e), which confirms the higher internal resistance in these large loading NiNb2O6 electrodes. The cycle life of the high loading NiNb2O6 electrode was also investigated and no capacity loss was observed after 100 cycles at a 1 C rate (Figure S12c, Supporting Information), which suggests that NiNb2O6 is a promising electrode material for practical applications for which high loading is required.

However, for NiNb2O6 to be applied as a fast-charging anode material in a real battery device, it needs to be combined with a standard cathode material commonly used in commercial lithium-ion batteries, such as LiFePO4 (LFP) and LiNi0.5Co0.2Mn0.3O2 (NCM811). The redox reactions during (de)lithiation in LFP, NCM811, and NiNb2O6 typically occur at 3.5, 3.9, and 1.7 V, respectively, resulting in the voltage plateaus when cycled against lithium metal (Figure S13a, Supporting Information). Therefore, the electrochemical behavior of the two different full cells was analyzed in different voltage ranges: the LFP[NiNb2O6] cell between 1.0 and 2.5 V and the NCM811[NiNb2O6] cell between 1.0 and 2.8 V. The voltage plateau of the LFP[NiNb2O6] cell is indeed at the expected 1.8 V (Figure 8a). Cycle life analysis of the LFP[NiNb2O6] cell at 5 C shows after 200 cycles a high specific capacity of 140.2 mAh g−1 and outstanding cycling stability with a capacity retention of 96.3% and a constant coulombic efficiency of about 99.8% (Figure S13b, Supporting Information). The rate performance analysis of the LFP[NiNb2O6] cell (Figure 8b) shows that by using NiNb2O6 as anode material, the full cell can cycle up to 20 C with 58 mAh g−1 capacity and 32.2% capacity retention as compared to 1 C. When comparing the 5 C cycling performance between the LFP[NiNb2O6] cell and an LFP[Li] cell (Figure 8c) it can be clearly observed that the cycling stability at such high rates is dramatically enhanced by replacing the lithium metal anode with our NiNb2O6 anode.

The rate performance and cycling stability of the NCM811[NiNb2O6] cell was also analyzed, and a voltage plateau was observed at the expected 2.05 V (Figure 8d). Cycle life analysis of the NCM811[NiNb2O6] cell after 1000 cycles at 5 C shows a high specific capacity of 117 mAh g−1 and outstanding cycling stability with a capacity retention of 88.8% and a coulombic efficiency between 99.8 and 100.2% (Figure S13c, Supporting Information). The NCM811[NiNb2O6] cell exhibited a lower capacity retention for higher rates (11% capacity retention at 20 C as compared to 1 C, Figure 8e), than the LFP[NiNb2O6] cell, which can be explained by a lower power density of the NCM811 commercial foil as compared to the LFP foil under high charging current densities. Comparison between the NCM811[NiNb2O6] cell and an NCM811[Li] cell (Figure 8f) shows that the cycling stability is also here strongly enhanced by introducing the NiNb2O6 anode.

Although the full cell studies show that using a NiNb2O6 electrode combines good cycling ability at high rates with a reasonable operating voltage range, it is still important to determine its electrochemical performance when applying a minimal amount of liquid electrolyte as required in commercial lithium-ion batteries. In order to investigate the electrochemical characteristics of NiNb2O6 electrodes under lean electrolyte conditions,[45] the amount of electrolyte was limited to 30 μL (mAh−1) in strong contrast to the used 300 μL (mAh−1) in the above experiments. The rate performance of NiNb2O6 in a half cell against lithium metal was still very good, as shown in Figure S14a, Supporting Information, for rates between 1 and 20 C. The voltage versus specific capacity profile during charge-discharge cycling at various rates shows that the average voltage plateau stays constant at around 1.7 V (Figure S14b, Supporting Information).
Information), while the voltage bias between the charge and discharge plateaus increased faster as compared to half cells with a larger amount of liquid electrolyte (Figure 5e). This indicates a faster increase in internal resistance when a minimal amount of electrolyte is used. However, when cycling at 5 C the coulombic efficiency was stable at 100.1% and the reversible capacity was still 115 mAh g$^{-1}$ after 600 cycles (Figure S14c, Supporting Information), demonstrating that NiNb$_2$O$_6$ electrodes also exhibit good cycling ability under lean electrolyte conditions.

3. Conclusions

In this work, nickel niobate NiNb$_2$O$_6$ has been demonstrated for the first time as a new high-rate anode material for lithium-ion batteries. The NiNb$_2$O$_6$ host crystal structure exhibits only a single type of channel for lithium-ion intercalation leading to a single voltage plateau at 1.6–1.7 V during charge-discharge cycling. The oxidation of all three transition metal ions (Ni, Nb) enables the structure to fully lithiate up to Li$_3$NiNb$_2$O$_6$ with a capacity of about 244 mAh g$^{-1}$ at low current densities. Nickel niobate exhibits a high diffusion coefficient of $10^{-12}$ cm$^2$ s$^{-1}$, which enables fast (dis)charging at high current densities resulting in high capacities of 220, 165, 140, and 50 mAh g$^{-1}$ for respectively 1, 5, 10, and 100 C. Furthermore, the minimal volume change during lithiation is the origin of the stable reversible lithiation process in NiNb$_2$O$_6$ and leads to a capacity retention of 81% after 20 000 cycles at 100 C. Finally, full cell systems against LiFePO$_4$ and NCM811 cathodes demonstrate the promising energy storage performance of nickel niobate anodes in practical battery devices. Our results strongly suggest that NiNb$_2$O$_6$ is an intrinsic high-rate anode material without the requirement of realizing nano-architectures as typical for numerous titanium- and niobium-based oxides through complex synthesis procedures to minimize the length scales for lithium diffusion.
4. Experimental Section

Material Synthesis: The NiNb$_2$O$_6$ powder was synthesized by a simple calcination process following a phase diagram study of this material system in 2005.[46] Niobium dioxide (99%, Alfa Aesar) and nickel oxide (99%, Sigma-Aldrich) powders in a molar ratio 1:1 were mixed for 24 h, and subsequently calcined at 1423 K for 2 h.

Material Characterization: The crystal structure of the synthesized NiNb$_2$O$_6$ powder was studied using X-ray diffraction (XRD, Bruker S8 Tiger WD) and Rietveld refinement with the FullProf program. The crystallinity, lattice parameters, and phase purity were evaluated. The specific surface area of the powder was measured by nitrogen adsorption-desorption isotherms using the Brunauer–Emmett–Teller (BET, Gemini VII 2375) method. The crystal structure and grain boundary formation was determined using X-ray source. The specific surface area was calculated using the BET method.

Electrochemical Analysis: Electrochemical measurements were performed in a galvanostat/dynamometric cell. The electrolyte was 1 M LiPF$_6$ in a 1:1 ratio (v/v) ethylene carbonate/dimethyl carbonate solution. The electrode was prepared by mixing the active material with conductive carbon (Super Pearls, 10% by weight) and a binder (PVDF, 5% by weight) using an ultrasonic mixer. The electrode was then pressed onto a current collector and dried in an oven. The electrochemical performance was characterized by cyclic voltammetry (CV) and galvanostatic charge-discharge measurements.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.
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