Chen H-Y, Friedl J, Pan C-J, Haider A, Al-Oweini R, Cheah YL, Lin M-H, Kortz U,
Hwang B-J, Srinivasan M, Stimming U.

[In situ X-ray absorption near edge structure studies and charge transfer
kinetics of Na₆\[V₁₀O₂₈\] electrodes.](#)

Physical Chemistry Chemical Physics 2017

DOI: <http://dx.doi.org/10.1039/C6CP05768C>

Copyright:

This is the authors' accepted manuscript of an article that was published in its final definitive form by Royal Society of Chemistry, 2017.

DOI link to article:

<http://dx.doi.org/10.1039/C6CP05768C>

Date deposited:

20/01/2017

Embargo release date:

16 January 2018

This work is licensed under a [Creative Commons Attribution-NonCommercial 3.0 Unported License](https://creativecommons.org/licenses/by-nc/3.0/)

In-situ X-ray Absorption Near Edge Structure Studies and Charge Transfer Kinetics of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ Electrodes

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Han-Yi Chen,^{a,b,c,d} Jochen Friedl,^{a,e} Chun-Jern Pan,^f Ali Haider,^g Rami Al-Oweini,^{g†} Yan Ling Cheah,^{c,h} Ming-Hsien Lin,^f Ulrich Kortz,^g Bing-Joe Hwang,^{f,i*} Madhavi Srinivasan,^{a,c,h*} and Ulrich Stimming,^{a,b,e*}

Polyoxometalates (POMs) have been reported as promising electrode material for energy storage applications due to their ability to undergo fast redox reactions with multiple transferred electrons per **polyanion**. Here we employ a polyoxovanadate salt, $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$, as electrode material in a lithium-ion containing electrolyte and investigate the electron transfer properties of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ on long and short timescales. Looking at equilibrated systems, in-situ V K-edge X-ray absorption near edge structure (XANES) studies show that all 10 V^{5+} ions in $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ can be reversibly reduced to V^{4+} in a potential range between $4 \sim 1.75 \text{ V}$ vs. Li/Li^+ . Focusing on the dynamic response of the electrode to potential pulses, the kinetics of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrodes and the dependence of the fundamental electron transfer rate k_0 on temperature are investigated. From these measurements we calculate the reorganization energy and compare it to theoretical predictions. The experimentally determined reorganization energy of $\lambda=184 \text{ meV}$ is in line with theoretical estimate and confirms the hypothesis of small values of λ for POMs due to electrostatic shielding of the redox center from the solvent.

Introduction

Polyoxometalates (POMs) are a class of transition metal oxide molecular clusters with well-defined structures. POMs have been reported to be promising electrode active materials for energy storage applications such as supercapacitors (SCs),¹⁻¹⁵ Li-ion batteries (LIBs), and Na-ion batteries (NIBs)¹⁶ due to their ability to undergo fast redox reactions and transfer

multiple electrons per **polyanion** while **retaining** their innate stability. The stability of a POM electrode is independent from the recoverability of its crystal structure, because the **polyanions** are expected to undergo redox process as a molecular cluster rather than a continuum.¹⁶⁻¹⁹

Many different POM materials have been studied for application in SCs.¹⁻¹⁵ A carbon nanotube/ $\text{Cs}_x\text{PMo}_{12}\text{O}_{40}$ hybrid material as electrode material for symmetric SCs with a Nafion 117 membrane previously activated with a sulfuric acid dissolution as solid electrolyte was reported by K. Cuentas-Gallegos et al., and exhibits high specific capacitance of 285 F g^{-1} with high energy density of 57 Wh kg^{-1} at a current density of 0.2 A g^{-1} .⁷ An asymmetric SC with polypyrrole/ $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ as positive electrode and poly(3,4-ethylenedioxythiophene)/ $\text{H}_3\text{PW}_{12}\text{O}_{40}$ as negative electrode in a $0.5 \text{ M H}_2\text{SO}_4$ aqueous electrolyte was reported by G. M. Suppes et al. showing device capacitance of 31 F g^{-1} with a maximum energy density of 4 Wh kg^{-1} and power density of 103 W kg^{-1} .⁹ We have reported a symmetric SC which combines single-walled carbon nanotubes (SWCNTs) with $([(\text{CH}_3(\text{CH}_2)_3)_4\text{N}]^+)_5[\text{PV}_2\text{Mo}^{\text{VI}}_{10}\text{O}_{40}]$ (**TBA-PV₂Mo₁₀**) as electrode material and displays high specific capacitance of 444 F g^{-1} , high energy density of 15.4 Wh kg^{-1} with high maximum power density of 15.7 W kg^{-1} in $1 \text{ M H}_2\text{SO}_4$ electrolyte.¹⁵ This **SWCNT-TBA-PV₂Mo₁₀** symmetric SC exhibits excellent long cycle life with capacitance retention of $\sim 95 \%$ after 6500 cycles.¹⁵ The most commonly used POMs in LIBs with Li-ion-containing organic electrolytes are molybdenum-based POMs such as $\text{TBA}_3[\text{PMo}_{12}\text{O}_{40}]$, $\text{K}_3[\text{PMo}_{12}\text{O}_{40}]$, and $\text{K}_4[\text{SiMo}_{12}\text{O}_{40}]$. High capacity of ca. 270 mAh g^{-1} can be achieved with

^a TUM CREATE, 1 CREATE Way, #10-02 CREATE Tower, 138602 Singapore

^b Department of Chemistry, Technische Universität München, Lichtenbergstraße 4, 85748 Garching, Germany

^c School of Materials Science and Engineering, Nanyang Technological University, 639798 Singapore

^d Department of Materials Science and Engineering, National Tsing Hua University, 101, Sec. 2, Kuang-Fu Road, Hsinchu 30013, Taiwan

^e School of Chemistry, Bedson Building, Newcastle University, Newcastle upon Tyne NE1 7RU, United Kingdom

^f Department of Chemical Engineering, National Taiwan University of Science and Technology (NTUST), Taipei 106, Taiwan

^g Department of Life Sciences and Chemistry, Jacobs University, P.O. Box 750561, 28725 Bremen, Germany

^h Energy Research Institute @ NTU (ERI@N), Research Techno Plaza, 50 Nanyang Drive, 637553 Singapore

ⁱ National Synchrotron Radiation Research Center (NSRRC), Hsinchu 30076, Taiwan

[†]Current address: Department of Chemistry, Faculty of Science, Beirut Arab University, P.O. Box 11 50 20, Riad El Solh 1107 2809, Beirut, Lebanon

E-mail: Ulrich.Stimming@newcastle.ac.uk, madhavi@ntu.edu.sg, bjh@mail.ntust.edu.tw

Electronic Supplementary Information (ESI) available: [SEM cross-section images of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrodes before and after cycling are shown in Figure S1. Normalized in-situ V K-edge XANES spectra for $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrodes are shown in Figure S2. XPS spectra of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ powder and electrodes before and after cycling are shown in Figure S3. The CV curves of the $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrode at various scan rates ranging from 0.1 to 2 mV s^{-1} , and the relation between peak currents (I_p) and square root of scan rate ($v^{0.5}$) are shown in Figure S4.]. See DOI: 10.1039/x0xx00000x

TBA₃[PMo₁₂O₄₀] as it stores up to 24 electrons in each **polyanion**.²⁰ However, the Mo-based POMs show poor capacity retention which might be due to the instability of [PMo₁₂O₄₀]³⁻ in the reduced state. N. Sonoyama and his group reported vanadium-based POMs, such as (KH)₉[PV₁₄O₄₂],²¹ K₇[NiV₁₃O₃₈],¹⁷ and K₇[MnV₁₃O₃₈],¹⁹ which exhibit high capacity (up to 200 mAh g⁻¹) and higher cycling stability than Mo-based POMs.

In the given scientific reports a transfer of multiple electrons per **polyanion** and high electron transfer rates are postulated. The latter is especially true for the SC studies as these devices rely on very fast processes to deliver high power densities. However, we are only aware of one study that determines the redox states of a POM used as active material in an energy storage device in-situ: H. Wang et al. reported an in-situ Mo K-edge X-ray absorption near edge structure (XANES) measurements on a Keggin-type POM, TBA₃[PMo₁₂O₄₀], and found a 24-electron transfer during the redox process.²⁰ It was detected that all 12 Mo^{VI} ions can be reduced to Mo^{IV}. At the same time, no systematic investigation of the electron transfer rates of POMs as electrode material was performed. There are kinetic studies for POMs in solution,²² but not for POMs as electrode material, as it was recently done for LiFePO₄.²³ In the present study of a V-based POM salt, sodium decavanadate Na₆[V₁₀O₂₈], we combine both XAFS spectroscopy and kinetic studies to obtain a complete understanding of the Na₆[V₁₀O₂₈] electron transfer. The polyhedral representation for the [V₁₀O₂₈]⁶⁻ anion is shown in **Figure 1**. XANES provides insights into variation of local structures and oxidation states during cycling of batteries.^{20, 24, 25}

We use XANES to determine the oxidation state of the V ions at different potentials. Comparing the valence of all V ions in the fully oxidized state (4.0 V vs. Li/Li⁺) and the fully reduced state (1.75 V vs. Li/Li⁺) indicates how many electrons were transferred when alternating between those potentials. Therefore, XANES give the thermodynamic equilibrium situation in an electrode.

On the other hand, kinetic studies reveal the dynamics of the electron transfer which is quantified in the electron transfer constant k_0 . They typically look at processes happening at a timescale of some milliseconds after the electrode potential is varied. Friedl et al. investigated the charge transfer kinetics of a tri-manganese substituted Keggin-based tungstosilicates [Mn^{III}₃(OH)₃(H₂O)₃(A- α -SiW₉O₃₄)]⁴⁻ (Mn^{III}₃SiW₉), dissolved in solution, by employing a chronoamperometric single pulse method at different temperatures.²² A value of $k_0 = 0.0032 \text{ cm s}^{-1}$ was found for the oxidation of solvated Mn^{III}₃ to Mn^{IV}₃. However, kinetic studies of POM as solid-state porous electrodes for energy storage applications have not been investigated so far. P. Bai et al. have reported a method to extract the charge transfer rates in carbon-coated LiFePO₄ porous electrodes from chronoamperometry experiments over a range of temperatures, and obtained a rate constant k_0 of $\sim 2 \times 10^{-4} \text{ s}^{-1}$ and a reorganization energy λ of $\sim 460 \text{ meV}$.²³ In order to determine the electron transfer rates and reorganization energy of Na₆[V₁₀O₂₈] porous electrodes, chronoamperometric

experiments are employed to obtain the transient currents at temperatures ranging from -10 °C to 50 °C.

Together the two complimentary studies, **XANES** and chronoamperometric experiments, give a comprehensive picture of the electron transfer of Na₆[V₁₀O₂₈]. For practical applications of Na₆[V₁₀O₂₈] as electrode material these studies are relevant as well. The information of number of transferred electrons from **XANES** is connected to the energy density; the electron transfer rate k_0 is tied to the power density that can be achieved by the battery.

Figure 1. Polyhedral representation for structure of [V₁₀O₂₈]⁶⁻ polyanion.

Results and discussion

Material and electrochemical characterization of Na₆[V₁₀O₂₈]

Na₆[V₁₀O₂₈] was characterized by ⁵¹V NMR and FTIR. The ⁵¹V NMR spectrum of [V₁₀O₂₈]⁶⁻ solution shows characteristic signals at -514 ppm, -500 ppm and -424 ppm which identifies the three different V environments in [V₁₀O₂₈]⁶⁻ polyanion as shown in **Figure 2a**, similar to previous studies.^{15, 16, 26, 27} The FTIR spectrum exhibits the characteristic absorption bands of Na₆[V₁₀O₂₈]. The vibrational mode of a V=O bond is located at 956 cm⁻¹.²⁸ The bands located at 837, 746, and 576 cm⁻¹ are assigned to V-O-V bridging as reported for [V₁₀O₂₈]⁶⁻ previously.^{15, 16, 28} The ratio of Na-V detected by inductively coupled plasma analysis is 0.59 which is the expected stoichiometry for Na₆[V₁₀O₂₈]. **The electronic conductivity of room-temperature-pressed bulk Na₆[V₁₀O₂₈] pellet was obtained as $\sim 10^{-6} \text{ S cm}^{-1}$ by DC polarization measurements. This value is much higher than for LiFePO₄ ($\sim 10^{-9} \text{ S cm}^{-1}$).²⁹** To understand the electrochemical properties of Na₆[V₁₀O₂₈] electrode, cyclic voltammetry, shown in **Figure 2c**, was carried out at a scan rate of 0.1 mV s⁻¹. The main oxidation peaks can be observed at 3.73 V, 2.90 V, 2.65 V, and 2.21 V vs. Li/Li⁺, corresponding reduction peaks are located at 3.71 V, 2.75 V, 2.40 V, and 2.24 V vs. Li/Li⁺. **The thickness of the electrodes before and after cycling (5 cycles, and measured at 1.75 V vs. Li/Li⁺) are similar (Figure S1), indicating the Na₆[V₁₀O₂₈] electrodes didn't undergo significant swelling during charge/discharge cycling.**

In-situ XANES analyses of Na₆[V₁₀O₂₈] Electrode

In situ XANES analysis was employed to detect the changes in the polyanion that are accompanied by oxidation and reduction. For SCs and battery applications, an important question is what oxidation states are involved and also how many of the vanadium ions undergo changes. This can be detected by XANES.

Figure 2. (a) ^{51}V NMR spectrum of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ dissolved in water. The $[\text{V}_{10}\text{O}_{28}]^{6-}$ polyanion structure is also shown and the magnetically inequivalent vanadium centers are indicated in different colors. (b) Cyclic voltammogram of a $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrode at 0.1 mV s^{-1} in $1 \text{ M LiPF}_6/\text{EC:DEC (1:1)}$ in a half-cell configuration with Li metal as counter electrode and reference electrode.

Figure 3a shows the V K-edge XANES spectra which were recorded at different potentials vs. Li/Li^+ from the first reduction to the second oxidation cycle. The data are normalized to edge steps in the XANES energy region. **Figure 3b** shows the energy range only from $5460 \sim 5510 \text{ eV}$ in order to distinguish the variation of V energy shift. The pre-edge baseline can be seen more clearly in the earlier energy region as shown in **Figure S2**. The energy shift during charge/discharge processes exhibits reversible processes.

The XANES spectra for the first cycle together with those of V_2O_5 (V^{5+}) and V_2O_4 (V^{4+}) as comparison are shown in **Figure 3b**. During reduction, the energy of the pre-edge peaks shifts to a lower energy which indicates that the valence of V is reduced from $5+$ to $4+$. When oxidized to 4 V , the energy of the pre-edge peaks shifts to higher energy which indicates the valence of V is oxidized from $4+$ to $5+$. V K-edge XANES absorption edge energies have been employed to identify the

valence of vanadium. By using the linear relationship between the V oxidation state and the X-ray absorption edge energy for the reference materials, V_2O_5 (V^{5+}) and V_2O_4 (V^{4+}), the averaged valence of the V ions in $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ can be calculated and plotted as a function of the battery potential. This is shown in **Figure 3c**. Prior to any electrochemical experiment the

Figure 3. (a) Normalized in-situ V K-edge XANES spectra for first reduction (1R, blue), first oxidation (1O, red), second reduction (2R, purple), and second oxidation (2O, pink) of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrodes. (b) V K-edge XANES spectra for $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrodes in the first cycle at potential of OCV (3 V), first full reduction (1R, 1.75 V), first full oxidation (1O, 4 V) compared with V_2O_5 and V_2O_4 reference materials. (c) Mean V valence of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrodes as a function of the cell voltage (V).

oxidation state of the 10 vanadium ions in $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ is expected to be V^{5+} . However, the initial average valence of the V before the first reduction (at open circuit voltage, ca. 3 V) is ca. 4.8.

The X-ray photoelectron spectroscopy (XPS) of as-synthesized $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ powder was performed as shown in **Figure S3**. The XPS spectra indicate that during the synthesis process (pH = 4.5), protons induced the partially reduction of $[\text{V}_{10}^{5+}\text{O}_{28}]^{6-}$ to $\text{H}_x[\text{V}_{10-x}^{5+}\text{V}_x^{4+}\text{O}_{28}]^{6-}$, and $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ powders was precipitated by adding ethanol which facilitated the formation of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ with both V^{5+} and V^{4+} oxidation states. During the first reduction cycle, the average valence of V decreases to ca. 4.0, and the first oxidation cycle increases the average valence of V 5.0. The second reduction and second oxidation cycle repeat that behaviour. The edge energy shifts during the first two redox cycles match each other indicating a fully reversible process. The change from 5.0 to 4.0 in the average valence of V during the reduction processes indicates that all 10 V^{5+} ions in $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ are reduced to V^{4+} which demonstrates that one $[\text{V}_{10}\text{O}_{28}]^{6-}$ polyanion can store 10 additional electrons. Ex-situ XPS measurements of the $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrodes before and after reducing to 1.75 V vs. Li/Li^+ are shown in **Figure S3**. V^{5+} was not reduced further than V^{4+} . V^{3+} and V^{2+} were not observed in the XPS spectra. The fact that V^{5+} still exists in the XPS spectra might be due to contact with air causing re-oxidation during transportation of the electrode for ex-situ XPS measurements. This result is as same as in literature.¹⁴ **Figure S4a** shows CV curves of the $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrode at various scan rates ranging from 0.1 to 2 mV s^{-1} . The relation between peak currents (I_p) and square root of scan rate ($v^{0.5}$) is illustrated in **Figure S4b**. The generated two straight lines indicate that the redox-processes are diffusion controlled ($I_p \propto v^{0.5}$),^{12, 15, 30, 31} and the involved freely diffusing species is most likely the lithium cation. Based on the results from V K-edge XANES absorption edge energies, the charge storage mechanism of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrode is dominated by the redox processes of vanadium accompanied by insertion/extraction of lithium ion according to the following equation:

Kinetic studies of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ Electrodes:

Kinetic studies were performed in order to see how fast changes in the polyanion are. XAS studies cannot elucidate this as they are done at equilibrium state. With chronoamperometric curves we analyzed the current response of an electrode to a potential pulse with a time resolution of 7.4 ms.

For a liquid-solid interface, the reorganization energy λ , which represents the required energy to change the nuclear configurations in the reactant and the solvent to those of the product state, can be predicted from first principles.³² The total reorganization energy for electron transfer consists of the outer reorganization of the solvent λ_o , contributed from long-range electrostatic forces, and the inner relaxation of the reactant λ_i , contributed from short range bond forces.²³ The

outer sphere reorganization λ_o energy of POMs is expected to be low because the POM framework shields the electrostatic interaction between redox-center and polar solvent.²² According to the Born energy of solvation, λ_o can be estimated by:²³

$$\lambda_o = \frac{e^2}{8\pi\epsilon_0 k_B T} \left(\frac{1}{a_0} - \frac{1}{2d} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (2)$$

where ϵ_0 is the permittivity of free space, a_0 the effective radius of the reactant, d the distance from the center of the reactant to the surface of the electrode, ϵ_{op} the optical dielectric constant and ϵ_s the static dielectric constant. Typically, λ_o represents the largest part of the total reorganization energy λ . With the average radius of $[\text{V}_{10}\text{O}_{28}]^{6-}$ $a_0 = 0.7$ nm and assuming direct contact of the $[\text{V}_{10}\text{O}_{28}]^{6-}$ with the electrode, i.e. $d = a_0 = 0.7$ nm, the calculated outer reorganization energy is 98 meV. This value is smaller than for a commonly used LIB cathode, LiFePO_4 (213 meV, FeO_6 octahedrons, $d = a_0 = 0.21$ nm).²³ To test whether this assumption of low reorganization energy is correct we determine λ experimentally by performing potential-step chronoamperometry experiments at temperatures ranging from -10 °C to 50 °C using a $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrode.

For electrode-electrolyte interfaces, Chidsey's method was used in many surface-bound redox systems in order to extract reaction rates from potential-step chronoamperometry experiments by fitting the linear relationship in the Tafel plots.³³ The transient current generated from a potential step can be fitted to a simple exponential decay:³⁴

$$I = e\Gamma k_{app} \exp(-k_{app}t) \quad (3)$$

where Γ is the coverage of the electrode and k_{app} is the single decay rate representing the rate of reactant consumption. However, equation (3) can be used only for flat electrodes with uniform reaction rates, such as the surface-bound monolayers of redox species, but not for porous electrodes or phase-transforming particles with non-uniform reaction rates.²³ In a porous electrode, the redox dynamics can be modelled as a simple three-state Markov chain with untransformed particles, active particles (transforming, partially intercalated with Li ions), and transformed particles (fully intercalated with Li ions).^{23, 35} As shown in **Figure 4**, we assume that the $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ porous electrode consists of $\text{Na}_6[\text{V}_{10}^{5+}\text{O}_{28}]$ particles (untransformed, yellow), active particles (transforming, grey), and $\text{Li}_{10}\text{Na}_6[\text{V}_{10}^{4+}\text{O}_{28}]$ particles (transformed, blue). k_A is the activation rate of each $\text{Na}_6[\text{V}_{10}^{5+}\text{O}_{28}]$ particle to transform into an activate particle. k is the reaction rate at the surface of active particles that continuously insert/extract lithium ions during redox process.^{23, 35}

Bai and Tian have reported a statistical model to characterize discrete-particle phase transformations in porous electrode recently.^{23, 35} The transient current in response to a potential step can be expressed as:²³

$$I = kQ \left[\frac{N_0 k + (N_1 - 1)k_A}{k - k_A} e^{-kt} + \frac{(1 - N_0 - N_1)k_A}{k - k_A} e^{-k_A t} \right] + I_0 e^{-t/\tau} \quad (4)$$

where Q is the capacity, N_0 is the initial fraction of reacting particles in the electrode. N_1 is the initial fraction of inactive particles in the electrode, which is set to zero in this work.²³ We added the contribution from non-faradaic currents that charge the double layer to this model: $I_0 e^{-t/\tau}$ with time constant τ and current at $t=0$ is I_0 .

In order to determine the electron transfer rates and reorganization energy of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrodes, chronoamperometry experiments were employed to obtain current transient. $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrodes were oxidized to 4.0 V vs. Li/Li^+ for 4 h before each negative over potential step and reduced to 2.0 V vs. Li/Li^+ for 4 h before each positive over

Figure 4. Schematic process in a porous electrode consisting of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ particles which will transform to active particles with an activation rate of k_A , active (transforming) particles, and $\text{Li}_{10}\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ particle which are transformed from an active particle with a reaction rate of k .

potential step in order to keep the same initial state. The value of the potential step was calculated based on the (temperature dependent) formal potential (e.g. 2.525 V vs. Li^+/Li at 25 °C) which was determined as the average of the main peak potentials of the cyclic voltammetry. The current transients were fitted to equation (4) to obtain values for k at various over potential. **Figure 5a** shows two exemplary current transients during a potential step of ± 125 mV at 25 °C. The fitted parameters for the oxidation step (125 mV) are $k = 0.094 \text{ s}^{-1}$, $k_A = 0.010 \text{ s}^{-1}$, $Q = 0.292 \text{ A s}$, $N_0 = 0.2$, and $I_0 = 5.9 \text{ mA}$, where the measured capacity is $Q_{\text{ex}} = 0.286 \text{ A s}$. The parameters for the reduction step (-125 mV) are $k = 0.09 \text{ s}^{-1}$, $k_A = 0.012 \text{ s}^{-1}$, $Q = 0.292 \text{ A s}$, $N_0 = 0.41$, and $I_0 = 94 \text{ mA}$, where the measured capacity is $Q_{\text{ex}} = 0.288 \text{ A s}$. The lower value for k_A than for k might be due to the amorphous structure of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ after initial discharge as observed from EXAFS results. The amorphous structure which lacks free channels for Li^+ diffusion might slow down the speed initial rate of starting Li ions intercalation (k_A).

Tafel plots of the reaction rates k extracted from chronoamperometric experiments using equation (4) are shown in **Figure 5b**, where $\eta = e(E - E^0)/k_B T$ is the dimensionless overpotential (e is the elementary charge, k_B is Boltzmann constant, and T is the absolute temperature). The electron transfer constant k_0 is obtained by extrapolating the linear fits to zero overpotential ($\eta = 0$).³⁶ Using the slopes in Fig. 8c to obtain a value for the transfer coefficient yields values of $\alpha < 0.1$ for both oxidation and reduction (assuming that one electron is transferred $n = 1$).

This k_0 value corresponds to the electron transfer of the whole $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ in which ten electrons participate, as shown by XANES. The kinetic rate constant for a single electron in $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ k_0' is obtained by dividing k_0 by the number of

Figure 5. (a) Examples of the transient currents with fitting curves at 25 °C. (b) Tafel plots of the reaction rates extracted by the transient current equation from chronoamperometry experiments of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrodes under 25 °C, where overpotential $\eta = e(E - E^0)/k_B T$. (c) Tafel plots of the fundamental reaction rates at -10, 10, 25, and 50 °C. (d) Arrhenius plot of the rate constants k_0' at -10, 10, 25, and 50 °C.

transferred electrons $n = 10$. The k_0' value of $\sim 6.0 \times 10^{-3} \text{ s}^{-1}$ for $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ is roughly 30 times higher than the one for LiFePO_4 ($k_0^{\text{LiFePO}_4} = 2.0 \times 10^{-4} \text{ s}^{-1}$) given in reference.²³

In order to determine the reorganization energy of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$, we varied the temperature from -10 °C to 50 °C. The reaction rates determined from experiments at -10, 10, 25, and 50 °C are shown in **Figure 5c**. According to the Arrhenius temperature dependence, the effective energy barrier, G_a , can be extracted by:

$$\ln k_0 = \ln A - \frac{G_a}{k_B T} \quad (5)$$

where A is the Arrhenius constant. The Arrhenius plots of the rate constants under -10, 10, 25, and 50 °C are displayed in **Figure 5d**. The effective energy barrier, G_a , of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ is ca. 49 meV as obtained from equation (5). This value is ~ 2.5 times lower than for LiFePO_4 in the literature ($G_a^{\text{LiFePO}_4} = 110 \text{ meV}$).²³ The effective energy barrier is close to $\lambda/4$ according to the classical Marcus theory:²³

$$G_a = \frac{(\lambda + \Delta G^0)^2}{4\lambda} \approx \frac{\lambda}{4} \quad (6)$$

Based on equation (6), the reorganization energy of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrode can be calculated as $\lambda = 197$ meV. This corresponds with our estimation for $\lambda_o = 98$ meV as $\lambda = \lambda_i + \lambda_o$. This indicates that $\lambda_i \approx 99$ meV and that λ_i and λ_o contribute roughly equal to the reorganization energy. Considering the size of the **polyanion** with its highly coordinated redox-centers this seems reasonable.

Conclusion

In this study, the electron transfer of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ was investigated by in-situ V K-edge **XANES** measurement and chronoamperometric experiments. The two experiments were chosen to investigate two very different time domains of the same process, oxidation and reduction of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$. In-situ V K-edge XANES measurements gave information on the electronic structure of the **polyanion** $[\text{V}_{10}\text{O}_{28}]^{6-}$ in its fully oxidized, fully reduced and three intermediate states. Chronoamperometric experiments gave information on the dynamic processes that occur at the electrode-electrolyte interface immediately after perturbing the system from steady state by a potential pulse. The electron transfer rate k_0 and, via the temperate dependence of the former, the effective energy barrier G_a experienced by the **polyanion** upon electron transfer could be determined. The two sets of experiments therefore gave complementary information that combined allow a new understanding of the electron transfer in the $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$. These findings are:

- The V^{5+} ions in $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ can be reversibly reduced to V^{4+} ions. During this process ten electrons are transferred (XANES);
- The difference in bond lengths between fully oxidized and fully reduced $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ are small and relatively reversible (EXAFS). This indicates that Li^+ ions do not intercalate into the structure but that the cations interact with surface of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$;
- The electron transfer of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ ($k_0 = 6.0 \times 10^{-3} \text{ s}^{-1}$) is roughly 30 times faster than that of LiFePO_4 ($k_0 = 2.0 \times 10^{-4} \text{ s}^{-1}$)²³ (Chronoamperometry and XANES);
- The fast electron transfer rates are enabled by a reorganization energy that is smaller than that of LiFePO_4 ($\lambda = 197$ meV compared to $213.3 \text{ meV} < \lambda^{\text{LiFePO}_4} < 347 \text{ meV}$). This finding agrees with our simple estimation of $\lambda_o \approx 98 \text{ meV}$.
- With this thorough understanding of the electron transfer properties the suitability of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ as electrode material in a LIB can be assessed:
- Ten electrons per **polyanion** result in a theoretical capacity of 245 mAh g^{-1} for $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$. This is higher than for typical LIB cathode materials such as LiCoO_2 (137 mAh g^{-1}) or LiFePO_4 (170 mAh g^{-1}).³⁷ Problematic for future high energy applications however is the relatively low redox potential of

2.55 V vs. Li/Li^+ which is lower than that of most other cathode materials;³⁸

- The electron transfer rate of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ is 30 times higher than that of LiFePO_4 . This is an indication that high power densities can be achieved with this material. This hypothesis is supported that we previously reported on a supercapacitor made from $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ that achieved up to 312 W kg^{-1} .¹⁴

Experimental Section

Synthesis and characterization of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$

$\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ was prepared using a literature method which is also reported in our previous studies.^{15, 16, 26} NaVO_3 (3 g) was dissolved in deionized water (100 mL). 4 M HCl was added to reduce the pH to 4.8. The solution was filtered and additional HCl reduced the pH further to 4.5. 200 mL of 95 % ethanol was added and resulted in precipitation of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ as orange solid powder which was isolated by filtration and air-dried. ⁵¹V NMR and FTIR are the two main techniques used to establish the identity of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$. The ⁵¹V NMR measurements were performed in 5 mm tubes at 105.4 MHz, and the spectra were recorded on a 400 MHz JEOL ECX instrument. A FTIR spectrophotometer (Perkin Elmer Frontier) was used to determine the infrared spectra using KBr pellets. The atomic ratio of sodium and vanadium of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ was detected by inductively coupled plasma spectroscopy (ICP) with a Dual-view Optima 5300 DV ICP-OES system. **The electronic conductivity of bulk $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ pellet was measured by DC polarization measurements (Bio-Logic SP300 potentiostat). The bulk $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ pellet was prepared by pressing the powder under 10 Pa at room temperature. The thickness was around 0.23 mm, and the area was 0.785 cm^2 .**

$\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrode preparation

The active material ($\text{Na}_6[\text{V}_{10}\text{O}_{28}]$) was mixed with poly(vinylidene fluoride) (PVDF) binder and carbon black (super P) in N-methylpyrrolidinone (NMP) with a weight ratio of 60 : 20 : 20 to prepare the active layer of the electrodes. The slurry was coated onto Al foil using a doctor blade; the electrode was then dried in air at 80 °C to remove the solvent. The coating was punched into pieces with diameter 16 mm and then roll-pressed. Subsequently, they were dried at 110 °C under vacuum for 4 hours. The film thickness is $\approx 22 \mu\text{m}$.

Electrochemical characterization and kinetic studies

Electrochemical measurements such as cyclic voltammetry and chronoamperometry were conducted in a half-cell configuration. The $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrodes were assembled in 2016 coin cells as the working electrode with a circular metallic lithium metal (diameter 16 mm) as counter and reference electrode, and glass fiber (Whatman, diameter 19 mm) as separator. 1M LiPF_6 in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 weight %) was employed as electrolyte. A Bio-Logic SP300 potentiostat was used to measure cyclic voltammetry and chronoamperometry.

Chronoamperometry experiments were conducted at -10 , 10 , 25 , 50 °C. $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrodes were kept at a potential of 4.0 V vs. Li/Li^+ for 4 h before each negative over potential step to ensure that the whole electrode is fully oxidized. Similarly, for positive over-potentials the electrode was maintained at 2.0 V vs. Li/Li^+ for 4 h. The size of the potential step was calculated according to the equilibrium potential E^0 , which was measured as the average of the mean peak potentials of the cyclic voltammetry at different temperatures.

In-situ XANES and ex-situ XPS measurement

The XANES analysis in this work aims to investigate the variation of V valence state at different charge-discharge states. The in-situ XANES cell was a modified 2016 coin cell with $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ as the working electrode (diameter 16 mm), circular metallic lithium metal (diameter 16 mm) as the counter electrode, and polyolefin (diameter 19 mm) as separator, as shown in **Figure S4**. The stainless steel cap, bottom, spacer, and spring were punched in order to generate windows for X-ray penetration. Those windows were covered with Kapton sealed by AB glue. 1M LiPF_6 in EC:DEC ($1:1$ weight %) was employed as electrolyte. In-situ V K-edge XAS spectra were carried out in transmission mode at room temperature using the beamline BL17C at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. The electronic accelerator of the storage ring supplied 1.5 GeV with an operating current of 360 mA. A Si double crystal monochromator was employed to perform an energy scan to adjust the parallelism and eliminate higher order harmonics. During in situ XANES measurements, the beam size on the electrode was limited to an area of 2×2 mm². The intensity of the incident and transmitted beams through the coin cell were detected by ionization chambers. The edge jumps for V of $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrodes were determined from the XANES spectra. The $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrodes were reduced from open circuit voltage (OCV, 3.0 V vs. Li/Li^+) to 2.75 , 2.40 , 2.25 , and 1.75 V vs. Li/Li^+ and then oxidized to 2.25 , 2.60 , 3.00 , 4.00 V vs. Li/Li^+ by providing constant current ($I = 25$ mA g⁻¹) at very low C rate (~ 0.1 C rate) without holding at those potentials to collect XANES data. We also measured XANES of the reference materials, commercial V_2O_5 (Aldrich, $\geq 98\%$) and V_2O_4 (Aldrich, $\geq 99\%$) powder, using the same measurement conditions. For the comparison of energy shift in XANES spectra, the pre edge subtractions and post-edge normalization have been carried out consistently and carefully. The XANES edge spectra were calibrated precisely to the first inflection point on the rising edge of the spectrum of a vanadium foil standard, which was assigned to 5464.0 eV, in every acquisition scan. High-resolution X-ray photoelectron spectroscopy (HR-XPS, PHI-5000 Versaprobe-II, ULVAC-PHI) was used to derive the oxidation states of the as-synthesized $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ powder and $\text{Na}_6[\text{V}_{10}\text{O}_{28}]$ electrodes before and after cycling and was carried out by using a monochromatic Al $\text{K}\alpha$ source. O $1s$ (530.0 eV) was used as reference.

Acknowledgements

This work was supported by TUM CREATE which is a joint research programme between Technische Universität München (TUM) in Germany and Nanyang Technological University (NTU) in Singapore with partial funding by the National Research Foundation of Singapore. Partial funding by National Taiwan University of Science and Technology, National Synchrotron Radiation Research Center, Newcastle University, and National Tsing Hua University is acknowledged. U. K. acknowledges the German Science Foundation (DFG KO-2288/20-1) and Jacobs University for research support, and A. H. thanks the German Academic Exchange Service (DAAD) for a PhD fellowship. H.-Y. C. acknowledges the Ministry of Science and Technology, R.O.C. (MOST 105-2218-E-007-025-MY3)

References

1. A. Yamada and J. B. Goodenough, *Journal of the Electrochemical Society*, 1998, **145**, 737-743.
2. P. Gomez-Romero, M. Chojak, K. Cuentas-Gallegos, J. A. Asensio, P. J. Kulesza, N. Casan-Pastor and M. Lira-Cantu, *Electrochemistry Communications*, 2003, **5**, 149-153.
3. A. M. White and R. C. T. Slade, *Synthetic Metals*, 2003, **139**, 123-131.
4. A. M. White and R. C. T. Slade, *Electrochimica Acta*, 2004, **49**, 861-865.
5. A. K. Cuentas-Gallegos, M. Lira-Cantu, N. Casan-Pastor and P. Gomez-Romero, *Advanced Functional Materials*, 2005, **15**, 1125-1133.
6. J. Vaillant, M. Lira-Cantu, K. Cuentas-Gallegos, N. Casan-Pastor and P. Gomez-Romero, *Progress in Solid State Chemistry*, 2006, **34**, 147-159.
7. A. Cuentas-Gallegos, R. Martinez-Rosales, M. Baibarac, P. Gomez-Romero and M. E. Rincon, *Electrochemistry Communications*, 2007, **9**, 2088-2092.
8. S. Park, K. Lian and Y. Gogotsi, *Journal of the Electrochemical Society*, 2009, **156**, A921-A926.
9. G. M. Suppes, C. G. Cameron and M. S. Freund, *Journal of the Electrochemical Society*, 2010, **157**, A1030-A1034.
10. G. Bajwa, T. Akter and K. Lian, in *Fullerenes, Nanotubes, and Carbon Nanostructures - 219th Ecs Meeting*, ed. D. Guldi, 2011, vol. 35, pp. 31-37.
11. G. Bajwa, Master of Applied Science Master thesis, University of Toronto, 2012.
12. V. Ruiz, J. Suarez-Guevara and P. Gomez-Romero, *Electrochemistry Communications*, 2012, **24**, 35-38.
13. G. Bajwa, M. Genovese and K. Lian, *Ecs Journal of Solid State Science and Technology*, 2013, **2**, M3046-M3050.
14. H.-Y. Chen, G. Wee, R. Al-Oweini, J. Friedl, K. S. Tan, Y. Wang, C. L. Wong, U. Kortz, U. Stimming and M. Srinivasan, *ChemPhysChem*, 2014, **15**, 2162-2169.
15. H.-Y. Chen, R. Al-Oweini, J. Friedl, C. Y. Lee, L. Li, U. Kortz, U. Stimming and M. Srinivasan, *Nanoscale*, 2015, **7**, 7934-7941.
16. S. Hartung, N. Bucher, H.-Y. Chen, R. Al-Oweini, S. Sreejith, P. Borah, Z. Yanli, U. Kortz, U. Stimming, H. E. Hoster and M. Srinivasan, *Journal of Power Sources*, 2015, **288**, 270-277.

17. E. F. Ni, S. Uematsu, Z. Quan and N. Sonoyama, *Journal of Nanoparticle Research*, 2013, **15**.
18. E. Ni, T. Kume, S. Uematsu, Z. Quan and N. Sonoyama, *Electrochemistry*, 2014, **82**, 14-18.
19. E. Ni, S. Uematsu and N. Sonoyama, *Solid State Ionics*, 2014.
20. H. Wang, S. Hamanaka, Y. Nishimoto, S. Irle, T. Yokoyama, H. Yoshikawa and K. Awaga, *Journal of the American Chemical Society*, 2012, **134**, 4918-4924.
21. S. Uematsu, Z. Quan, Y. Suganuma and N. Sonoyama, *Journal of Power Sources*, 2012, **217**, 13-20.
22. J. Friedl, R. Al-Oweini, M. Herpich, B. Keita, U. Kortz and U. Stimming, *Electrochimica Acta*, 2014, **141**, 357-366.
23. P. Bai and M. Z. Bazant, *Nature Communications*, 2014, **5**.
24. H. Wang, S. Hamanaka, T. Yokoyama, H. Yoshikawa and K. Awaga, *Chemistry-an Asian Journal*, 2011, **6**, 1074-1079.
25. J.-H. Cheng, C.-J. Pan, J.-F. Lee, J.-M. Chen, M. Guignard, C. Delmas, D. Carlier and B.-J. Hwang, *Chemistry of Materials*, 2014, **26**, 1219-1225.
26. P. J. Domaille, *Journal of the American Chemical Society*, 1984, **106**, 7677-7687.
27. S. Ramos, R. O. Duarte, J. J. G. Moura and M. Aureliano, *Dalton Transactions*, 2009, 7985-7994.
28. V. D. K. Zhetcheva and L. P. Pavlova, *Turkish Journal of Chemistry*, 2011, **35**, 215-223.
29. M. Park, X. Zhang, M. Chung, G. B. Less and A. M. Sastry, *Journal of Power Sources*, 2010, **195**, 7904-7929.
30. J. M. Li, K. H. Chang and C. C. Hu, *Electrochemistry Communications*, 2010, **12**, 1800-1803.
31. J. Chen, S. L. Liu, W. Feng, G. Q. Zhang and F. L. Yang, *Physical Chemistry Chemical Physics*, 2013, **15**, 5664-5669.
32. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd Edition, Wiley Global Education, USA, 2000.
33. C. E. D. Chidsey, *Science*, 1991, **251**, 919-922.
34. M. C. Henstridge, E. Laborda, N. V. Rees and R. G. Compton, *Electrochimica Acta*, 2012, **84**, 12-20.
35. P. Bai and G. Y. Tian, *Electrochimica Acta*, 2013, **89**, 644-651.
36. E. Laborda, M. C. Henstridge, C. Batchelor-McAuley and R. G. Compton, *Chemical Society Reviews*, 2013, **42**, 4894-4905.
37. N. Nitta, F. Wu, J. T. Lee and G. Yushin, *Materials Today*, 2015, **18**, 252-264.
38. J. M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359-367.