Vanadate–Borate Glasses for Rechargeable Li-ion Batteries: New High Capacity Cathode Materials

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V2O5 based materials are attractive cathode alternatives due to the many oxidation state switches of vanadium bringing up a high theoretical specific capacity. However, significant capacity losses are eminent for crystalline V2O5 phases related to the irreversible phase transformations and/or vanadium dissolution starting from the first discharge cycle. These problems can be circumvented if amorphous or glassy vanadium oxide phases are employed. Here, we demonstrate vanadate-borate glasses as high capacity cathode materials for rechargeable Li-ion batteries for the first time. The composite electrodes of V2O5 – LiBO2 glass with reduced graphite oxide (RGO) deliver specific energies around 1000 Wh/kg and retain high specific capacities in the range of ~300 mAh/g for the first 100 cycles. V2O5 – LiBO2 glasses are considered as promising cathode materials for rechargeable Li-ion batteries fabricated through rather simple and cost-efficient methods.

After the introduction of LiFePO4 as a positive electrode material for LIBs, the focus of research in this field lies mainly on poly-anionic materials. However, the low theoretical capacity of LiFePO4 (170 mAh/g) is a setback for its applications in batteries requiring high energy densities. This constraint is exemplified by the limited range of electric vehicles (~< 160 km) hindering their large scale introduction. To increase energy densities, novel cathode materials beyond NMC, LFP and etc. have to be developed which utilize more than one Li per 100 atomic mass units. Owing to the many accessible oxidation states of vanadium, vanadate-based electrodes could become interesting alternatives. Consequently, there has been extensive research in order to employ on vanadates as a cathode materials that are synthesized by various methods resulting different morphologies, compositions and properties. With the use of thin film electrodes and relatively low current rates, the insertion of up to 5.8 and 4 Li per formula unit of V2O5 were demonstrated for aerogels 1,2 and xerogels 3–6, respectively. A single phase process was claimed for the lithiation mechanism of the xerogel-based cathodes on the observation of a steady decrease of the voltage in the discharge curve accompanied by the reduction of V5+ to lower oxidation states1,7. The high amount of lithium insertion that was stated for such thin film samples decreases to ca. 2–3 Li per V2O5 when standard electrodes and higher rates (~>C/2) are used1,8. For crystalline counterparts, V2O5 transforms into several LixV2O5 phases depending on the amount of lithium inserted, α- (x < 0.01), ω- (0.35 < x < 0.7), δ- (x = 1), γ- (1 < x < 2) and ω- (x = 3)10. The phases that are formed by intercalation up to one Li per formula unit of V2O5 (α-, γ-, δ-Li, V2O5) are not significantly different from the initial structure, but only a puckering of VO5 pyramid layers occurs. These phases can be cycled in a reversible way with a theoretical capacity of ~147 mAh/g. In contrast, an irreversible phase transformation arises on insertion of more than 0.5 Li per V2O5 and γ-Li2V2O5 is formed that can be cycled without structural transformation in the range of 0 ≤ x ≤ 2. This process yields a theoretical capacity of ~294 mAh/g. Upon deep discharge to voltages below 1.9 V, another irreversible transition occurs to ω-Li4V2O5 with an insertion of 3 Li per formula unit10. With this, a large theoretical capacity of ~440 mAh/g is reached that is almost three times larger than that of many conventional cathode materials. ω-Li4V2O5 cycles like a single solid solution in subsequent charge/discharge curves with an irreversible capacity loss in the first charge since all of the inserted lithium atoms cannot be extracted from the host structure (~0.4 Li per formula unit of Li4V2O5 remain unexchanged)10. The capacity retention is a huge problem as half of the capacity vanishes within the first ten cycles for the unaltered V2O5 even at very low current rates (10 mA/g)11. Bulk V2O5 is also considered to be kinetically limited by its low ionic and electronic conductivities and it has been shown that the increase of current density leads to markedly reduced practical capacities11,12.
In order to address these problems, many different approaches have been tried by various research groups. Whittingham et al. employed nanorods of V$_2$O$_5$ that were synthesized by annealing xerogels under O$_2$ atmosphere, and obtained a stable capacity of ca. 300 mAh/g but only for the first 10 cycles\(^{13,14}\). The enhanced performance of this material was attributed mainly to its high surface area, shorter Li diffusion lengths and facilitation of strain relaxation\(^{13,14}\). Porous monodisperse V$_2$O$_5$ microspheres were tested by Wang et al. in the voltage window of 2.05–4.0 V, and an initial discharge capacity of 276 mAh/g was realized with a fading rate of 0.38% per cycle\(^{15}\). Composite electrodes with carbon and conducting polymers were also tried. A V$_2$O$_5$/polypropylene-composite cathode prepared by Kim et al. delivered an initial discharge capacity of ~425 mAh/g that decreased to ~250 mAh/g till the 10th cycle\(^{16}\). For a nano-V$_2$O$_5$/PEDOT composite film electrode, Song et al. reported specific capacities of ~262, 239, 186 and 141 mAh/g at 0.1C, 1C, 10C and 100C rates within 4.0–1.8 V, respectively\(^{17}\). Numerous other reports employing nano-particles and composite electrodes can be found in the literature\(^{18–21}\).

Irreversible phase transformations and volume work leading to amorphization as well as to loss of low valence state metal ions into the electrolyte accompany most high capacity materials during cycling. To tackle these problems, we have chosen borate-based glasses of V$_2$O$_5$ in order to explore vitreous redox-active systems pursuing the goal of utilizing many oxidation states of vanadium to the highest possible extent and fixing the vanadate group by a network former to enhance cycling stability. There are a few research reports on V$_2$O$_5$–P$_2$O$_5$ glasses as cathode materials\(^{22–24}\). Sakurai et al. reported a first discharge capacity of 500 mAh/g within 4.0–1.0 V for the V$_2$O$_5$–P$_2$O$_5$ glass cathode\(^{25}\). The cathode material functions as a uniform material without any visible plateau, but the capacity on the first charge already drops to 350 mAh/g, and cycling properties are not very remarkable for the large potential window. For borate based binary, ternary, quaternary V$_2$O$_5$ glass systems, there had been research on vibrational, mechanical, thermal and electrical properties\(^{25–30}\). The use of V$_2$O$_5$–B$_2$O$_3$ glass as an electrode material for secondary batteries is mentioned in a few older patents grosso modo together with other glasses\(^{31,32}\), however, no electrochemical study exploring their actual utilization exists in literature, yet. Furthermore, to the best of our knowledge, V$_2$O$_5$–LiBO$_2$ glasses (Li$_2$O–B$_2$O$_3$–V$_2$O$_5$ system) and their composites have not been explored as positive electrode material yet, and here, we report on V$_2$O$_5$–LiBO$_2$ glasses and their composites as cathode materials for rechargeable Li-ion batteries for the first time. The composite electrode of V$_2$O$_5$–LiBO$_2$ glass with reduced graphite oxide delivers first discharge capacities around 400 mAh/g and maintain capacities in the range of ~300 mAh/g within the first 100 cycles. The synthesis method for the new class of electrodes is very simple and cost efficient. Comparable cathode materials delivering similar capacities and specific energies are only obtainable by laborious synthetic methods and using expensive techniques and educts.

**Results & Discussion**

Here, a glassy material from the Li$_2$O–B$_2$O$_3$–V$_2$O$_5$ glass system, which will be referred to as V$_2$O$_5$–LiBO$_2$ glass in the following text, is reported as a cathode material for rechargeable LIBs. A mixture of 80 wt-% V$_2$O$_5$ and 20 wt-% LiBO$_2$ is melted at 900°C. The subsequent quenching to room temperature produces the glass material. Elemental analysis performed using inductively coupled plasma optical emission spectrometry (ICP-OES) confirmed the final composition of the glass material that is in close proximity to the intended glass composition (80 wt-% V$_2$O$_5$–20 wt-% LiBO$_2$) (Table S1). Based on this composition, a theoretical capacity of ~118 mAh/g is expected for the insertion or extraction of 1 Li per formula unit of V$_2$O$_5$–LiBO$_2$ glass.

The XRD powder pattern of the V$_2$O$_5$–LiBO$_2$ glass material is shown in Fig. 1a. In the XRD pattern, the glassy product exhibits a high background lacking any Bragg reflections. The differential thermal analysis (DTA) proves the glassy nature of the quenched 80–20 wt-% V$_2$O$_5$–LiBO$_2$ material (Fig. S1). The endothermic effect at ~205°C arises from the glass transition, followed by transformations into crystalline phases around 218°C and 325°C that are indicated by exothermic peaks. The melting region for the crystalline phases corresponds to a range of ~550–650°C, as it can be estimated from the heating curve.

Fig. 1b depicts infrared (IR) spectra of the V$_2$O$_5$–LiBO$_2$ glass and the educts, V$_2$O$_5$ (99.2%, Alfa Aesar) and LiBO$_2$ (99.9%, Alfa Aesar). The IR spectrum of the V$_2$O$_5$–LiBO$_2$ glass is very different from the spectra of the educts proving the formation of a new kind of material. The strong band observed for V$_2$O$_5$ at ca. 1020 cm$^{-1}$ stemming from the stretching mode of the vanadyl group $\nu$ = O in the VO$_5$ square pyramids disappears in the spectrum of the V$_2$O$_5$–LiBO$_2$ glass probably indicating the loss of localized double bond. A weak band emerging at ~970–980 cm$^{-1}$ could still be attributed to the stretching of $\nu$ = O with a decrease in bond order, but this band together with the ones at ~890–900 cm$^{-1}$ and ~1090–1100 cm$^{-1}$ could also be assigned to the asymmetric stretching vibrations of BO$_3$ tetrahedral units that are expected to appear between 850 and 1100 cm$^{-1}$\(^{32–35}\). This finding also fits well with the influence of alkali metal oxide addition into borate glass: The addition of an alkali metal oxide (e.g. Li$_2$O) to borate glasses was discussed to alter the glass network by the conversion of trigonal BO$_3$ groups from the boroxol rings to BO$_4$ groups; thus, increasing the number of structural linkages through B – O – B bonds\(^{36,37}\). Though some BO$_3$ groups are converted to tetrahedral units, they are still present in the glass network as the bands observed between 1200 and 1600 cm$^{-1}$ are related to the asymmetric stretching modes of BO$_3$ trigonal units\(^{33,38}\).

Scanning electron microscopy (SEM) images of the V$_2$O$_5$–LiBO$_2$ glass are displayed in Fig. 2. When the glass forming melt is quenched, a homogeneous disk of glass is obtained. Fig. 2a depicts a side image of V$_2$O$_5$–LiBO$_2$ glass disk with a thickness of ~200 microns. The homogenous nature can also be observed under an optical microscope with a gleaming purple appearance similar to volcanic glass. These large glass pieces have to be ground in order to make further characterizations and to form electrodes of the material. The particles can be crushed down to a spread between micron and sub-micron size (Fig. 2b) in an agate mortar by extensive grinding. Yet, some large pieces of 40–50 microns in size are still present (Fig. 2b).

Micron-sized blocks of the glass material can be seen in transmission electron microscopy images (TEM) (Fig. 2c). As revealed by bulk characterization techniques, the state is mostly amorphous being further verified here with a lack of order even at 5–10 nm resolution for many parts of the sample (Fig. 2d). Electron diffraction patterns lacking any reflections further support the glassy nature of the material (Fig. S2). However, lattice fringes with a spacing of about 9.5 Å extending into nano-crystallites with sizes in the range of 20–30 nm are also found in some regions (Fig. S3). The d-distance (~9.5 Å) corresponds to 2θ = ~9.3, where a broad reflection from Li$_2$V$_4$O$_9$ phases (ICSD 166482) appears, in the XRD powder pattern of the V$_2$O$_5$–LiBO$_2$ glass, if heated above the glass transition temperature (Fig. S4). Thus, it can be concluded that self-ordering nano-crystallites of Li$_2$V$_2$O$_5$ are embedded in the amorphous glass matrix.

For a typical fabrication of the V$_2$O$_5$–LiBO$_2$ glass electrode, (70 wt%- active material, (20 wt%- conductive carbon (Super P® Timcal) and (10 wt%-) PVDF binders were manually mixed in an agate mortar without any ball-milling. The cells built from such electrodes were tested in a galvanostatic mode by first discharging to 1.5 V and then charging to 4.0 V at a rate of 50 mA/g. The reported specific capacities here are based on the active mass of
V₂O₅ – LiBO₂ glass; not exclusively on the mass of V₂O₅. The first ten galvanostatic charge/discharge curves of the RGO/V₂O₅ – LiBO₂ glass investigated here. Fig. 3b shows the rate capability for the RGO/V₂O₅ – LiBO₂ glass composite. Transmission electron microscopy images (TEM) reveal more information on covering and interaction of the V₂O₅ – LiBO₂ glass with reduced graphite oxide (RGO). Some parts of the glass material are directly coated by only a few layers of RGO as shown in Fig. 2e & Fig. S5. Widespread coating provided by the flocculated RGO is also observed (Fig. S7). The interlayer distance found for the flocculated RGO, ~ 4.3 Å, and also, the XPS characterization of the RGO/V₂O₅ – LiBO₂ glass composite provide further evidence for the partial reduction of graphite oxide and the formation of RGO on glass particle surfaces (Fig. S8 & S10). Both the direct RGO coating of the glass surfaces and clustering of RGO between the V₂O₅ – LiBO₂ glass particles, respectively, are expected to improve short and long range conductivity within the composite electrode.

The cells with a cathode composition of ~ 74 wt-% active material, ~ 16 wt-% conductive carbon originating from the RGO (no additional carbon black) and ~ 10 wt-% PVDF were cycled between 1.5 V and 4.0 V at a rate of 50 mA/g. Similar to the plain glass material, the reported specific capacities for the composite electrode are calculated based on the active mass of V₂O₅ – LiBO₂ glass; not exclusively on the mass of V₂O₅ and RGO is considered as an inactive part in the potential window of our interest, as well. The first ten galvanostatic charge/discharge curves of the RGO/V₂O₅ – LiBO₂ glass composite are shown in Fig. 4a. The first discharge capacity has been raised to ~ 405 mAh/g for the composite electrode. This capacity corresponds to the insertion of 1.5 V₄ species in the glass material. A high capacity of ~ 390 mAh/g is reached in the subsequent charge proving that the RGO/V₂O₅ – LiBO₂ glass composite also does not suffer from the large irreversible capacity loss associated with the phase transformation of crystalline V₂O₅. Remarkably, this initial charge capacity is largely preserved in the range of ~ 300 mAh/g within the first 100 cycles (Fig. 4c). If the cell is charged to 4.5 V first, the glass material can be also delithiated resulting a first charge capacity of ~ 20–25 mAh/g; however, the cycling stability is found to be rather poor in the large potential window (Figure S12 & S13). The electrochemical activity in the first charge also indicates the presence of the partially reduction of V⁵⁺ species to V⁴⁺ species in the glass material. Based on the obtained first charge capacity, the formation of Li₁₀.₃V₂O₅ phases above the glass transition, XPS and magnetic measurements (Fig. S9, S10 and S11), the averaged oxidation state for vanadium in the glassy electrode materials can be given as ~ 4.8–4.9 +. The sloping characteristic of the galvanostatic charge/discharge curves again indicates a homogeneous phase process. The rate capability for the RGO/V₂O₅ – LiBO₂ glass composite has been enhanced as well. Fig. 4b shows the rate capability within first 50 galvanostatic cycles between 1.5 V and 4.0 V. For rates of 50, 100, 200 and 400 mA/g, average discharge capacities are ~ 388, 355, 329 and 299 mAh/g, respectively. When the rate is changed back from 400 mA/g to 50 mA/g, the discharge capacity recovers from 298 mAh/g to ~ 370 mAh/g at the 42nd cycle. The specific energy is ~ 900 Whkg⁻¹ with an average discharge voltage of ~ 2.4 V at this
cycle. The favorable response of the electrochemical system to higher charge/discharge rates demonstrates the improvements arising from the composite electrode. The capacity delivered at the highest rate (400 mA/g) is more than doubled compared to the amount obtained for the V$_2$O$_5$ – LiBO$_2$ glass electrode without RGO. The improvement made with ball-milling and conductive coating is encouraging as it shows that the problem is mainly stemming from the kinetic problems associated with the larger glass particles. Clearly, further optimization of the electrochemical performance can be expected by improving the composite characteristics.

Discussion

The galvanostatic cycling analysis of vanadate – borate glasses shows featureless curves without any distinct voltage plateau starting from the first discharge; this supports the understanding of a glassy electrode material. Similar to the other V$_2$O$_5$ based amorphous cathode materials$^{4-9}$, more than 3 Li per formula unit can be inserted to vanadate-borate glass electrodes. The amorphous nature of the glass electrodes is also largely preserved upon lithium insertion and extraction (Fig. S14); however, further investigations that are beyond the scope of this current work could be performed to deeply understand the lithiation/delithiation processes. Nevertheless, the notable electrochemical properties for vanadate – borate glasses are mainly attributed to the absence of a long range order that allows for subtle structural adaptations, which cannot occur within crystalline phases. This is markedly different from the huge capacity loss observed for crystalline V$_2$O$_5$ phases in the first cycle related to the irreversible phase transformation to α-Li$_2$V$_2$O$_5$, which cannot be cycled to its full extent within 1.5–4.0 V. Besides, crystalline phases tend to deteriorate during large redox work showing itself as capacity fading under extensive cycling$^{12-15,38-40}$. The borate glass former constitutes a kind of glue to low valence vanadium species, too. Thus, well-known problems of crystalline V$_2$O$_5$ electrodes can be circumvented in a glassy vanadium oxide electrode. Furthermore, the RGO/V$_2$O$_5$ – LiBO$_2$ glass composite provides a much enhanced electrochemical performance. This can be traced back to a number of reasons: 1. In comparison to the other composite electrodes with reduced graphite oxide$^{41-43}$, there are common features arising from the RGO network that is expected to facilitate Li$^+$ ion as well as electron transports, prevent contact losses under extensive cycling and may act as a protective layer against cycling by-products. 2. In addition to common characteristics with previously demonstrated systems, a much finer coating of particles is found for the V$_2$O$_5$ – LiBO$_2$ glass with only a few layers of RGO. 3. The direct coating of the surface and the network formation via reduced graphite oxide seemingly improves short and long range conductivity, respectively. 4. Effects of particle size are also very prominent for the V$_2$O$_5$ – LiBO$_2$ glass system, as noticeably better kinetic properties are attained for smaller particles in terms of a decreased polarization and a better rate capability.

In conclusion, vanadate-borate glasses have been demonstrated as inexpensive, high capacity cathode materials for the first time. The RGO/V$_2$O$_5$ – LiBO$_2$ composite electrode delivers first discharge capacities around 400 mAh/g and maintains high capacities in the range of ~300 mAh/g for the first 100 cycles (between 1.5 V and 4.0 V at 50 mA/g rate)! The rate capability of the composite electrode is also notable with a discharge capacity of ~299 mAh/g (35th cycle) at 400 mA/g rate. Clearly, higher charge/discharge capacities and enhanced cycling stabilities compared to bulk and various nano-forms of V$_2$O$_5$ have been demonstrated here for vanadate – borate glasses. For practical battery applications, the overall cycling stability may still be improved via better cell and electrode engineering.
the exploration of different protective coatings and more stable electrolyte systems. Nevertheless, the results obtained for vanadate–borate glasses are very encouraging and may trigger further studies for similar glass systems that could encompass the practical use of glassy materials as next generation electrode materials for rechargeable Li-ion batteries.

**Methods**

**Synthesis of V₂O₅ – LiBO₂ glass and reduced graphite oxide (RGO) composite.** V₂O₅ – LiBO₂ glass was obtained with a glass forming procedure. V₂O₅ (99.2%, Alfa Aesar) and LiBO₂ (99.9% Alfa Aesar) analytical pure grades in corresponding amounts (e.g. 4 g V₂O₅ and 1 g LiBO₂ for 80: 20 wt-% V₂O₅ : LiBO₂) were thoroughly mixed and ground in an agate mortar, and thereafter, the mixtures were placed in Pt crucibles. The crucibles were heated in a muffle furnace at 900 °C and homogeneous melts were obtained after 30–60 min. of heat treatment. Then, melts were quenched between Cu plates yielding V₂O₅ – LiBO₂ glass. The produced glass disks were pulverized in an agate mortar for further characterizations. The composite with reduced graphite oxide was prepared by ball-milling ~66.6 wt-% active material with ~33.3 wt-% graphite oxide that was followed by the heat treatment for the reduction (9 hours under Ar atmosphere at 200 °C). The final carbon content of the composite material was found to be ~18 wt-% by combustion-infrared spectroscopy analysis (LECO instruments, ETH LOC Micro-Laboratory).

**Characterization.** Powder X-ray diffraction patterns of the samples were acquired with a STOE Stadi P diffractometer equipped with a germanium monochromator and CuKα radiation (40 kV, 35 mA). Differential thermal analysis (DTA) was performed with a NETZSCH STA 409 C/CD. Samples were planted in Pt crucibles, and heating/cooling curves between room temperature and 930 °C were obtained under air flow. FT-IR spectra were recorded with a Thermo Scientific Nicolet iS10 Smart iTR. Scanning electron microscopy (SEM) analysis of samples were carried out with a Zeiss Gemini 1530 operated at 1 kV. Transmission electron microscopy (TEM) analysis was performed with a Tecnai F30 microscope (FEI; field emission gun), operated at 500 kV, point resolution of 5 m. X-ray absorption near-edge structure (XANES) measurements were performed with a beam line X30C at the Advanced Photon Source, Argonne National Laboratory. XPS spectra were collected with a SPECS PHOIBOS 100 analyzer using a non-monochromatic X-ray source (Al Kα: 1486 eV). Due to the charge shift, the binding energy was re-calibrated using the O1s peak set to 530.0 eV.

**Electrochemical tests.** Fabrication of composite materials with RGO, no additional carbon black was used, and (90 wt-%) composite powder was thoroughly mixed with (10 wt-%) PVDF binder in an agate mortar. The mixture was ultrasonically dispersed in 1:4 toluene : THF solution. The resulting slurry was cast on Ti current collectors and dried at 80 °C under vacuum. The dried electrodes had approximately 5 mg electrochemically active material (a loading of ~4–5 mg/cm²).

Figure 3 | (a) The first ten charge/discharge curves of the V₂O₅ – LiBO₂ glass within a potential window of 1.5–4.0 V at 50 mA/g rate, (b) the rate capability of the V₂O₅ – LiBO₂ glass within 1.5–4.0 V at 50, 100, 200 and 400 mA/g rates (at room temperature).

Figure 4 | (a) The first ten charge/discharge curves of the RGO/V₂O₅ – LiBO₂ glass composite in a potential window of 1.5–4.0 V at 50 mA/g rate, (b) the rate capability of the RGO/V₂O₅ – LiBO₂ glass composite within 1.5–4.0 V at 50, 100, 200 and 400 mA/g rates (at room temperature), (c) discharge capacity vs. cycle number for the RGO/V₂O₅ – LiBO₂ glass composite within 1.5–4.0 V at 50 and 100 mA/g rates.
usual rate of 50 mA/g. Rate capability tests were done with ~ 10 cycle blocks at varying rates: 50, 100, 200, 400 mA/g, and then again 50 mA/g; the rates were successively altered after a charging session. The reported specific capacities were calculated based on the active mass of V₂O₅ - LIBO; glass not exclusively on the mass of V₂O₅.

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Author contributions

S.A. and R.N. planned the research project; S.A. conducted the experiments. F.K. did XPS analysis-characterization. S.A. wrote the main manuscript text and prepared figures, and all authors reviewed the manuscript.

Additional information

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