Abstract: An electronically active glass has the composition \((T\text{g}O_2)_{x} - (M\text{g}O_2)_{y} - (Na/LiB_0)_z\), wherein \(T\) is a transition metal selected from V and Mo, M is a metal selected from Ni, Co, Na, Al, Mn, Cr, Cu, Fe, Ti, and mixtures thereof, \(x, y, z, u, v\) are stoichiometric coefficients resulting in a neutral compound, \(z = 2y/(\text{oxidation state of } T)\) and \(u = 2v/(\text{oxidation state of } M)\), \(w\) and \(t\) are weight-%, wherein \(z\) is 70-80, \(w\) is 0-20, \(t\) is 10-30, and the sum of \(z, w\), and \(t\) is 100 weight-%, in particular \(V_0.5\text{LiB}_0\) and \(V_0.5\text{NiO-LiB}_0\).
V2O5-L1BO2, V2C>5-NiO-LiB02 glasses and their composites obtained by nitrogen doping and reduced graphite oxide blending as cathode active materials

Cross References to Related Applications

This application claims the priority of European patent application EP12158829 filed on March 9, 2012 and the disclosure of which is incorporated herein in its entirety.

Technical Field

This invention regards glasses comprising electronically/electrochemically (later on referred to as electronically) active cathode materials, in particular such materials for use in rechargeable cells.

Background Art

At present, Li-ion batteries have mostly L1MO2 (M= Co, Ni, Mn, or combination of these transition metals) cathodes and graphite based anodes. The use of such oxide materials as cathode materials is a setback because of aspects like high cost, low stored energy density and stability. In recent years, LiFePC>4 was introduced as a cathode material. This material provided a major improvement and was regarded as the solution for the large scale applications of Li-ion batteries. LiFePC>4 operates at 3.5 V with the theoretical capacity of 170 Ah/kg. The PO₄³⁻ units comprised therein are fixing oxygen in the structure thereby stabilizing the structure. Lacking stability is a problem for L1MO2 cathodes acting as strong oxidizing agents for organic
electrolytes. LiFePO₄ became a very interesting and popular material, as approx. 1000 papers were published about LiFePO₄ in the last five years, and a number of companies started to produce and commercialize LiFePO₄ and its composites. However, there is still a large energy density demand required for several applications, like for electric vehicles, and current cathode materials are away from satisfying this demand. Materials with higher specific energy and capacity need to be developed to enable e.g. the large scale use of plug-in electric vehicles.

V₂O₅ based compounds could be good alternatives for the current cathode materials, and there has been extensive research on V₂O₅ as a cathode material synthesized by various methods resulting in different morphologies and properties [1-3]. V₂O₅ theoretically should deliver a capacity of approx. 440 Ah/kg [2] for exchange of three lithium. However, the bulk material is limited by low ionic and electronic conductivity [4], and the major problem for both bulk and nano-V₂C₅ is irreversible capacity loss upon cycling.

As V₂O₅ partially transforms into ω-phase (Li₃V₂C₅) upon cycling (LiₓV₂C₅ phases are depending on the amount of lithium inserted, a-phase (x < 0.01), ε-phase (0.35 < x < 0.7), δ-phase (x = 1), γ-phase (1 < x < 3) and ω-phase (x = 3)) [1, 2], an irreversible capacity loss occurs already in the first discharge and the theoretical capacity cannot be reached in subsequent cycles, i.e. once the ω-phase is formed this phase remains even upon withdrawal of the lithium. These problems could be reduced with amorphous-glass V₂O₅ systems, as some researchers already tried with V₂O₅ - P₂O₅ glass as a cathode material [5]. Also for boron trioxide (B₂O₃) based binary, ternary, quaternary V₂O₅ glass systems, there had been research on vibrational, mechanical, thermal and electrical properties [6-9]. However, the own experiments with boron trioxide revealed...
that no glass could be obtained at up to 30 wt-% B2O3. Therefore it was the aim of the present invention to provide a boron based glass comprising a low amount of glass forming material or a high amount of cationic active material, respectively.

Disclosure of the Invention

Hence, it is a general object of the invention to provide a glass with low boron content that is suitable as cathode active material.

Now, in order to implement these and still further objects of the invention, which will become more readily apparent as the description proceeds, the glass is manifested by the features that it has the composition

$$(T_xO_y)_z - (M_uO_v)_w - (Na/LiB_2O_3)_t$$

wherein

$T$ is a transition metal selected from $V$ and $Mo$,

$M$ is a metal selected from $Ni$, $Co$, $Na$, $Al$, $Mn$, $Cr$, $Cu$, $Fe$, $Ti$ and mixtures thereof,

$x$, $y$, $u$, and $v$ are the stoichiometric coefficients resulting in a neutral compound, i.e. $x = 2y/(\text{oxidation state of } T)$ and $u = 2v/(\text{oxidation state of } M)$,

$z$, $w$ and $t$ are weight-%, wherein

$z$ is 70-80,

$w$ is 0-20,

$t$ is 10-30, and

the sum of $z$, $w$ and $t$ is 100 weight-%.

Li/NaBC>2 means that the cation may be Li or Na or combination thereof.

To the inventors knowledge so far, there has been no research on glasses of the above identified type and composites comprising such glasses as cathode materials for Li-ion batteries.
In general $T_xO_y$ is selected from the group consisting of MoO$_3$ or V$_2$O$_5$ or mixtures thereof, and preferably is V$_2$O$_5$, and $M_uO_v$ is selected from the group consisting of NiO, Co$_3$O$_4$, Na$_2$O, Al$_2$O$_3$, MnO, Mn$_2$O$_7$, Cr$_2$O$_3$, CuO, Ni$_2$O$_3$, Fe$_2$O$_3$, TiO$_2$, etc. and mixtures thereof, wherein Co$_3$O$_4$ proved less good than NiO in electrochemical respect.

Na$_2$O, Al$_2$O$_3$, MnO, Mn$_2$O$_7$, Cr$_2$O$_3$, CuO, Ni$_2$O$_3$, Fe$_2$O$_3$, TiO$_2$, etc. and mixtures thereof, in particular Na$_2$O and/or Al$_2$O$_3$ may improve structural stability while maintaining the high specific energy and capacity.

In one embodiment $w$ is 0. A presently preferred glass of this type is V$_2$O$_5$ - LiBO$_2$ glass, in particular V$_2$O$_5$ - LiBO$_2$ (80/20) glass with (80/20) designating 80 wt-% V$_2$O$_5$ and 20 wt-% LiBO$_2$, i.e. $z$ is about 80, $w$ is about 0 and $t$ is about 20.

Another embodiment is a glass wherein $z$ is about 80, $w$ is about 5 and $t$ is about 15.

In one embodiment wherein $w$ is not 0, $M_uO_v$ is NiO or $C_3$O$_4$ with NiO being preferred.

In another embodiment wherein $w$ is not 0, $M_uO_v$ is Na$_2$O or Al$_2$O$_3$.

It is also possible to prepare and use mixtures of $T_xO_y$ and/or $M_uO_v$. Mixtures of $M_uO_v$ with (i) NiO and (ii) Na$_2$O and/or Al$_2$O$_3$ are preferred.

In a preferred embodiment, Li/NaBO$_2$ is LiBO$_2$.

The cycling stability may be enhanced by nitrogen doping via Li$_3$N treatment. In case of non lithium liberating anodes like a graphite anode doping provides an additional advantage in that the glass is enriched with Li.

The glassy material of the present invention may comprise minor amounts of crystalline particles of electronically active material. These incorporated particles usually and preferably have particle sizes in the nano range, e.g. from 20 to 30 nm, while the glassy particles are in the range of 200 nm to 3μm, preferably
200 nm to 2 µm, more preferred 200 nm to 1 µm and most preferred are in the submicron range.

An additional object of the present invention is a cathode material (composite) comprising a glass of any of the preceding claims together with carbon and/or graphite, in particular carbon and/or graphite obtained by reduction of graphite oxide, and optionally a binder.

Also an object of the present invention is a method for producing a glass as described above, said method comprising providing a composition by mixing, optionally and preferably with grinding, of z wt-% of T<sub>x</sub>O<sub>y</sub> and w wt-% M<sub>x</sub>O<sub>y</sub> and t wt-% Na/LiBC<sub>&gt;2</sub> and heating the mixture to a temperature where a melt is formed but preferably not over 900°C for a time sufficient to form a homogeneous melt, such as for 1 hour, followed by fast cooling (quenching), e.g. between copper plates. For systems that tend to form paramagnetic phases at higher temperatures like the binary system V2C<sub>&gt;5</sub>-LiB02 performing the reaction at lower temperature like a temperature up to 800°C, may be favourable.

Optionally and preferably the quenching step is followed by a milling step (e.g. a ball-milling step) in order to arrive at preferred particle sizes.

Further objects of the invention are a cathode comprising the glass or the cathode material of the present invention on a current collector and a rechargeable battery comprising such a cathode as well as an anode, a diaphragm and an electrolyte.

For producing such cathode, the cathode material is slurried in a small amount of solvent, applied to the current collector and then the solvent is removed by drying. With small amount of solvent an amount is meant that is sufficient to provide a slurry suitable to be applied onto a current collector, usually an amount of about 1 to 2 ml/g glassy material, at most about 5 ml/g.
Brief Description of the Drawings

The invention will be better understood and objects other than those set forth above will become apparent when consideration is given to the following detailed description thereof. Such description makes reference to the annexed drawings, wherein the Figures show:

Figure 1: XRD powder pattern of 80-20 wt-% V2O5 - LiBO2 glass.

Figure 2: Electron microscope images of pulverized 80-20 wt-% V2C>5-LiBO2 glass with

Figure 2.1: SEM images of pulverized 80-20 wt-% V2C>5-LiBO2 glass.

Figure 2.2: TEM images of 80-20 wt-% V205 - LiBC>2 glass.

Figure 3: Galvanostatic (50A/kg rate) cycling (0th to 10th) of 80-20 wt-% V205-LiBO2 glass.

Figure 4: XRD powder pattern of the V2O5 - LiBO2 glass composite material.

Figure 5: Differential thermal analysis of 80-20 wt-% V205 - LiBO2 glass.

Figure 6: Electron microscope images of V205-LiBC>2 glass composite material with

Figure 6.1: SEM images of the V205-LiBO2 glass composite material.

Figure 6.2: TEM images of the V205-LiBO2 glass composite material.

Figure 7: Galvanostatic measurements with

Figure 7.1: Galvanostatic (50A/kg rate) cycling (0th to 90th) of the V205-LiBO2 glass-redGO (reduced graphite oxide) composite. The first discharge capacity is ~ 350 Ah/kg and reversible cycling around 300 Ah/kg (between 1.5 - 4.0 V) with decreases in subsequent cycles (ca. 250 Ah/kg at 90th cycle). The cycling properties and the initial discharge capacity is considerably improved compared to plain V2C>5-LiBO2 glass.
Figure 7.2: Galvanostatic (25A/kg rate) cycling (0\textsuperscript{th} to 42\textsuperscript{nd}) of the V2O5-L1BO2 glass-redGO composite. The battery was first charged to 4.5 V and a capacity of 20 Ah/kg was obtained (Lithium extraction in the 1\textsuperscript{st} charge was not possible for the plain V2O5-L1BO2 glass). The first discharge capacity was approx. 400 Ah/kg. Reversible cycling between 1.5-4.5 V resulted in decreases in subsequent cycles. The capacity and the voltage range dropped drastically through the 40\textsuperscript{th} cycle.

The battery was first charged to 4.5 V and a capacity of 20 Ah/kg was obtained (Lithium extraction in the 1\textsuperscript{st} charge was not possible for the plain V2O5-L1BO2 glass).

Then cycling was performed between 1.5 - 4.0 V. At 60\textsuperscript{th} cycle, the specific energy was ~ 2.51V for discharge and ~ 2.96V for charge. These are ca. 0.3 V higher than the V2C>5-LiB02 glass system indicating the contribution of NiO addition.

Figure 8: XRD powder pattern of the V2O5-N1O-LiBC>2 glass composite material.

Figure 9: Electron microscope images of the V2C>5-NiO-LiB02 glass composite material wherein

Figure 9.1: SEM images of the V2C>5-NiO-LiB02 glass composite material.

Figure 9.2: TEM images of the V2C>5-NiO-LiB02 glass composite material.

Figure 10: Galvanostatic cycling at a rate of 25A/kg (0\textsuperscript{th} to 24\textsuperscript{th}) of the V\textsubscript{2}O\textsubscript{5}-NiO-LiB0\textsubscript{2} glass composite material. OCV = 3.50 V, cycling 4.5 - 1.5 V, ~ 8.5 Ah/kg capacity on the 1\textsuperscript{st} charge to 4.5 V, and first discharge capacity was ~ 435 Ah/kg. Then cycling between 1.5 - 4.5 V. At 20\textsuperscript{th} cycle the charge capacity was ~ 372 Ah/kg and the discharge capacity ~ 376 Ah/kg.

Figure 11: Specific energy vs. cycle number plot for the V2C>5-NiO-LiB02 glass composite material (cycling between 4.5-1.5 V at 25A/kg). High specific energy with polarization at 20\textsuperscript{th} cycle ~ 1100 Wh/kg for charge and ~ 950 Wh/kg for discharge. The average voltage was ~ 2.51V for discharge and ~ 2.96V for charge. These are ca. 0.3 V higher than the V2C>5-LiB02 glass system indicating the contribution of NiO addition.

Figure 12: Galvanostatic cycling at a rate of 50A/kg (0\textsuperscript{th} to 60\textsuperscript{th}) of the V\textsubscript{2}O\textsubscript{5}-NiO-LiB0\textsubscript{2} glass composite material. OCV = 3.51 V, in the first discharge to 1.5 V a specific capacity of ~ 380 Ah/kg was obtained. Then cycling was performed between 1.5 - 4.0 V. At 60\textsuperscript{th}
cycle the charge capacity was ~ 275 Ah/kg and the discharge capacity ~ 265 Ah/kg.

Figure 13: XRD powder pattern of the nitrogen doped V2C>5-NiO-LiB02 glass composite material.

Figure 14: TEM images of the nitrogen doped V2C>5-NiO-LiB02 glass composite material.

Figure 15.1: Galvanostatic cycling at a rate of 25A/kg (0th to 10th) of the nitrogen doped V2O5-N1O-LiBC>2 glass composite material. OCV = 3.16 V, cycling between 4.5 - 1.5 V. ~ 77 Ah/kg capacity was obtained on the 1st charge to 4.5 V proving the chemical lithiation achieved by the reaction with Li3N. The first discharge capacity was ~ 362 Ah/kg. Further cycling was performed between 1.5 - 4.5 V. At 8th cycle the charge capacity was ~ 378 Ah/kg and the discharge capacity ~ 375 Ah/kg.

Figure 15.2: Galvanostatic cycling at a rate of 50A/kg (0th to 20th) of the nitrogen doped V2O5-N1O-LiBC>2 glass composite material. OCV = 3.16 V, the first discharge capacity was ~ 291 Ah/kg. Further cycling was performed between 1.5 - 4.0 V. At 20th cycle the charge capacity was ~ 277 Ah/kg and the discharge capacity ~ 275 Ah/kg.

Figure 16: Specific energy vs. cycle number plot for different glass composite materials of the present invention (cycling between 1.5 - 4.0 V at 50 A/kg).

Modes for Carrying out the Invention

General Remark: Wherever capacities are mentioned these capacities are for the glass composite material and would be higher when calculated only for the comprised vanadium oxide.

Example 1: V2O5 - L1BO2 glass:
The V2O5-L1BO2 glass system is interesting because completely glassy material can be obtained with
only 20 wt-% LiBC>2, which was not possible with B2O3 as the glass former in earlier trials. A V2O5-LiB02 glass delivering high specific capacity is shown here for the first time as well as its use as cathode material for Li-ion batteries.

Although glassy materials with more than 20 wt-% LiB02 can easily be obtained and are also within the scope of the present invention, glasses with as low as possible LiB02 content are preferred in view of maximized content of electronically active material.

Synthesis:

80-20 wt-% V2O5-LiB02 glass was obtained with a glass synthesis procedure. V2O5 and LiB02 analytical pure grade powders in corresponding amounts were thoroughly mixed and ground in an agate mortar, and the mixtures were placed in a Pt crucible. The crucible with the material was put in a muffle furnace at 900°C, and the desired melt was obtained after 1 hour of heat treatment. The melt was quenched in air between Cu plates and V2C>5-LiB02 glass was formed. Dependent on possible delays during quenching, it is also possible to obtain glass ceramics including crystallites of partially lithiated V2O5 (Li_xV2O5) or LiV3C>5.

The V2O5-LiB02 glass was pulverized in an agate mortar in order to make analytical measurements. The powder had a green-brown color.

Characterization:

XRD powder diffraction:

The XRD powder pattern of the V2O5-LiB02 glass is illustrated in Figure 1. The product was glassy, but the diffraction peaks at 2θ ~ 26.5 and 27.8 could be attributed to trace amounts of Li_xV2C>5.
SEM-TEM:
SEM and TEM images of 80-20 wt-% V₂O₅-L₁BO₂ glass are given in Figure 2 with Figure 2.1 being SEM images of pulverized 80-20 wt-% V₂O₅-L₁BO₂ glass and Figure 2.2 being respective TEM images. The electron microscopy images revealed that the material had mostly non-crystalline parts. But the particle sizes still were in the micron range. By milling methods, like ball milling, the particle sizes can be further reduced, preferably from the size obtained in Example 1 which is 1 to 20 microns for most particles with some large particles in the range of 40 to 50 µm to about 200 nm to 3 µm or smaller such as at most 2 µm or 1 µm. Crystalline particles that may be incorporated within the glass such as LiₓV₂C>5 usually are in the range of 20 to 30 nm.

Magnetic measurement:
The magnetic measurements showed that 80-20 wt-% V₂O₅-L₁BO₂ glass synthesized at 900°C had paramagnetic behaviour. The paramagnetic behaviour could be attributed to the formation of lower oxidation states of vanadium at 900°C by the loss of oxygen in the system. The glass synthesized at 700°C had a yellowish color, whereas the one obtained at 900°C was more greenish-brown, which is also an indication for the formation of lower oxidation state. Thus, the glass should be synthesized at temperatures below 900°C, preferably at 800°C or less.

Electrochemical Characterization:
The working electrode was 7:2:1 (w/w/w) V₂O₅-L₁BO₂ (80/20) glass / Super ® conductive carbon / polyvinylidene fluoride (PVDF). The materials were mixed and ground in an agate mortar and the mixture was added into a small amount of 4:1 THF:Toluene solvent mixture. With small amount an amount is meant that is sufficient to provide a slurry suitable to be applied onto a current
collector, usually an amount of about 1 to 2 ml/g glassy material, at most about 5 ml/g. The slurry was spread on a titanium (Ti) current collector and dried at 85°C for 3 hours under vacuum. The active material on the current collector was approx. 3-6 mg at the end of the process.

The battery cell was constructed using lithium metal as an anode, 1 M solution of LiPF₆ in 1:1 ethylene carbonate/dimethyl carbonate (EC/DMC) as an electrolyte, and polypropylene film as a separator. The cells were charged-discharged with a rate of 50 A/kg between 1.5V and 4V. The galvanostatic measurement for V₂O₅ - LiB₀₂ glass is depicted in Figure 3.

Example 2: V₂O₅ - LiB₀₂ glass - reduced graphite oxide (redGO) composite:

A composite electrode material of V₂O₅ - LiB₀₂ glass is obtained by the reduction of graphite oxide to graphite and amorphous carbon in a mixture of the glass and graphite oxide. The composite electrode material gives higher practical specific capacity, and the cycling is much improved compared to plain V₂O₅ - LiB₀₂ glass.

Synthesis:

20wt-% graphite oxide and 80 wt-% V₂O₅-LiB₀₂ were ball-milled together and the resulting mixture was heated at 200°C for 8 hours under N₂ flow or in air to ensure the reduction of graphite oxide to graphite and amorphous carbon. The carbon content was found to be 10.9 wt-% at the end of the process.

Characterization:

XRD powder diffraction and DTA:

After ball-milling and heat treatment, a black powder was obtained. No diffraction peak from graphite oxide or graphite was observed. The absence of a graphite peak was attributed to the thin layers formed.
The crystallinity of the material was enhanced by heat treatment with the formation of Li$_x$V$_2$C$_{>5}$ phases (see Figure 4). The formation of these phases could also be tracked by differential thermal analysis with the exothermic peak at about 200°C (see Figure 5).

SEM-TEM:

SEM and TEM images of the composite material are given in Figure 6, wherein Figure 6.1 shows SEM images of the V$_2$O$_5$ - LiB$_2$O$_3$ glass composite material and Figure 6.2 respective TEM images. The graphite flakes and carbon on the surface of V$_2$O$_5$-LiB$_2$O$_3$ can be seen in the electron microscopy images.

Electrochemical Characterization:

The working electrode used was 9:1 (w/w) composite material/polyvinylidene fluoride (PVDF), which can be also given as approx. 81 wt-% active material (V$_2$C$_{>5}$-LiB$_2$O$_3$ glass), 9 wt-% conductive carbon and 10 wt-% PVDF. The materials were mixed and grinded in an agate mortar and the mixture was added into a small amount of 4:1 THF:Toluene solvent mixture. The slurry was spread on a Ti current collector and dried at 85°C for 3 hours under vacuum. The active material on the current collector was ca. 3-6 mg at the end of the process. The battery cell was constructed using lithium metal as an anode, 1 M solution of LiPF$_6$ in 1:1 EC/DMC as an electrolyte, and polypropylene film as a separator. The cells were charged-discharged with a rate of 50 A/kg between 1.5V and 4V (or 4.5V). The galvanostatic measurement for the composite material is depicted in Figure 7.

Figure 7.1 illustrates galvanostatic cycling at a rate of 50A/kg (0$^{th}$ to 90$^{th}$ cycles) of the V$_2$O$_5$-LiB$_{>2}$ glass-redGO composite (redGO designates reduced graphene oxide). The first discharge capacity was approx. 350 Ah/kg and for reversible cycling (between 1.5 - 4.0
V) was around 300 Ah/kg with decreases in subsequent cycles (ca. 250 Ah/kg at 90th cycle). The cycling properties and the initial discharge capacity was considerably improved compared to plain V2O5-LiB02 glass.

Figure 7.2 illustrates galvanostatic cycling at a rate of 25A/kg (0th to 42nd cycle) of the V2O5-LiB02 glass-redGO composite. The battery was first charged to 4.5 V and a capacity of 20 Ah/kg was obtained (Lithium extraction in the 1st charge was not possible for the plain V2C>5-LiB02 glass). The first discharge capacity was about 400 Ah/kg and reversible cycling between 1.5-4.5 V resulted in decreases in subsequent cycles. The capacity and the voltage range dropped drastically through 40th cycle.

Example 3: V2C>5-MnO-LiB02 glass - reduced graphite oxide composite, in particular V2C>5-NiO-LiB02 glass - reduced graphite oxide composite:

In order to improve the voltage range of the glass system ternary and quaternary glass systems of the inventive type, in particular V2O5 glass systems where LiB02 is used as the glass former, can be synthesized with M in MnO being high voltage redox couples, such as Co2+/Co3+ and Ni2+/Ni3+. As an alternative or in combination with the high voltage redox couples the structural integrity upon cycling can be improved by incorporating a compound like Na2O and/or Al2O3 as it was previously shown for NMC (nickel-mangan-cobaltoxide) materials.

V2O5-Na2O-LiB02, V2O5-CO30 4-LiB02, V2O5-Co304-Al2O3-LiBC>2, and V2C>5-NiO-LiB02 glasses were successfully synthesized. Among these systems, the best results so far were obtained with V2C>5-NiO-LiB02. Therefore V2C>5-NiO-LiB02 is further described below.
Synthesis:

80-5-15 wt-% \( V_{2}O_{5}-NiO-LiB_{2}O_{2} \) glass was obtained as described before. \( V_{2}O_{5} \), NiO and LiBO\(_2\) analytical pure grade powders in corresponding amounts were thoroughly mixed and grinded in an agate mortar, and the mixtures were placed in a Pt crucible. The crucible with the material was put in a muffle furnace at 900 °C. The melt was obtained after 1 hour of heat treatment. The melt was quenched in air between Cu plates and \( V_{2}C>5-LiB_{2}O_{2} \) glass was formed.

To obtain the composite material, 33.3 wt-% graphite oxide and 67.7 wt-% \( V_{2}O_{5}-NiO-LiB_{2}O_{2} \) glass were ball-milled together and the resulting mixture was heated at 200°C for 8 hours in \( \frac{3}{4} \) flow or air flow to ensure the reduction of graphite oxide to graphite and amorphous carbon. The carbon content was found to be 18.5 wt-% at the end of the process.

Characterization:

XRD powder diffraction:

The XRD powder pattern of the 80-5-15 wt-% \( V_{2}C>5-NiO-LiB_{2}O_{2} \) glass composite material is illustrated in Figure 8. Both the initial glass and the composite material obtained after treatment with graphite oxide were amorphous and differing from the \( V_{2}O_{5}-LiB_{2}O_{2} \) system. No diffraction due to \( Li_{x}V_{2}C>5 \) phases was observed.

SEM-TEM:

SEM and TEM images of the composite material are given in Figure 9, wherein Figure 9.1 shows SEM images of the \( V_{2}C>5-NiO-LiB_{2}O_{2} \) glass composite material, and Figure 9.2 shows respective TEM images. The graphite flakes and carbon on the surface of \( V_{2}C>5-NiO-LiB_{2}O_{2} \) glass can be seen in the electron microscopy images. The presence of nickel and vanadium are confirmed by the EDX spectrum (not shown); though the boron was not detected in the EDX spectrum due to the background, the presence
can be seen in the EELS spectrum at approx. 200 eV (not shown).

Electrochemical Characterization:

The working electrode used was 72.5 wt-% active material (V2C>5-NiO-LiBO2 glass), 17.5 wt-% conductive carbon and 10 wt-% PVDF. The materials were mixed and ground in an agate mortar and the mixture was added into a small amount of 4:1 THF: Toluene solvent mixture (e.g. 2 ml solvent per g glass). The slurry was spread on a Ti current collector and dried at 85°C for 3 hours under vacuum. The active material on the current collector was approx. 3-6 mg at the end of the process. The battery cell was constructed using lithium metal as an anode, 1 M solution of LiPF6 in 1:1 EC/DMC as an electrolyte, and polypropylene film as a separator. The cells were charged-discharged with a rate of 50 or 25 A/kg between 1.5V and 4V (or 4.5V). The galvanostatic cycling for the V2C>5-NiO-LiBO2 glass composite material at a rate of 25A/kg (0th to 24th cycle) is shown in Figure 10. OCV was 3.50 V, cycling was performed from 4.5 - 1.5 V, capacity on the 1st charge to 4.5 V was ~ 8.5 Ah/kg, the first discharge capacity was ~ 435 Ah/kg. Then cycling between 1.5 - 4.5 V was performed. At 20th cycle the charge capacity was ~ 372 Ah/kg and the discharge capacity ~ 376 Ah/kg.

Figure 11 is a plot of specific energy vs. cycle number for the V2C>5-NiO-LiBO2 glass composite material (cycling between 4.5-1.5 V at 25A/kg) showing high specific energy with polarization at 20th cycle ~ 1100 Wh/kg for charge and ~ 950 Wh/kg for discharge. The average voltage was ~ 2.51V for discharge and ~ 2.96V for charge. This is about 0.3 V higher than the V2C>5-LiBO2 glass system indicating the contribution of NiO addition.

Figure 12 shows galvanostatic cycling at a rate of 50A/kg (0th to 60th cycle) of the V2O5 -NiO-LiBC>2 glass composite material. OCV was 3.51 V, first discharge
to 1.5 V resulted in a specific capacity of ~ 380 Ah/kg. Then cycling was performed between 1.5 – 4.0 V. At 60th cycle the charge capacity was ~ 275 Ah/kg and the discharge capacity ~ 265 Ah/kg.

5 Example 4: N-doped V2C>5-NiO-LiB02 glass – reduced graphite oxide composite

The performance of the V2O5-L1B02 glass systems has been improved step by step with (i) NiO doping and (ii) the composite electrode formation via graphite oxide treatment. However, the polarization and the cycling stability, though it could be considerably improved with these means, still was an object for further improvement. Nitrogen doping and chemical lithiation by the reaction of glass with Li3N was found to further decrease these problems by mainly increasing the conductivity of the system.

Below, nitrogen doping and chemical lithiation with Li3N is shown for V2C>5-NiO-LiB02 glass composite material, but it can be applied to other V2O5-LiB>2 glass systems as well.

Synthesis:

33.3 wt-% graphite oxide, 67.7 wt-% V2C>5-NiO-LiB02 glass, and 3.3 wt-% Li3N were ball-milled together under Ar atmosphere and the resulting mixture was heated at 200°C for 8 hours under N2 flow to ensure the reduction of graphite oxide to graphite and amorphous carbon. The carbon and nitrogen content were found to be -18.9 wt-% and ~ 0.45 wt-% at the end of the process by elemental analysis.
Characterization :
XRD powder diffraction :

The XRD powder pattern of the nitrogen doped 80-5-15 wt-% V2C>5-NiO-LiB02 glass composite material is shown in Figure 13. The composite material obtained after treatment with graphite oxide and Li3N was amorphous, and no diffraction peaks due to graphite oxide and Li3N were observed.

TEM:

TEM images of the composite material are given in Figure 14 showing graphite flakes and carbon on the surface of V2C>5-NiO-LiB02 glass particles.

Electrochemical Characterization :

The working electrode used was 73 wt-% active material (nitrogen doped and chemically lithiated V2O5-NiO-LiBC>2 glass), 17 wt-% conductive carbon and 10 wt-% PVDF. The materials were mixed and grinded in an agate mortar and the mixture was added into a small amount of 4:1 THF:Toluene solvent mixture. A small amount of solvent mixture refers to an amount that makes the slurry spreadable onto the current collector and may be about 2 ml/g active material. The slurry was spread on a Ti current collector and dried at 85°C for 3 hours under vacuum. The active material on the current collector was approx. 3-6 mg at the end of the process. The battery cell was constructed using lithium metal as an anode, 1 M solution of LiPF6 in 1:1 EC/DMC as an electrolyte, and polypropylene film as a separator. The cells were charged-discharged with a rate of 50 or 25 A/kg between 1.5V and 4V (or 4.5V). The galvanostatic measurement for the composite material is depicted in Figure 15, wherein Figure 15.1 shows galvanostatic cycling at a rate of 25A/kg (0th to 10th cycle) of the nitrogen doped V2O5-NiO-LiBC>2 glass composite material and Figure 15.2 shows galvanostatic cycling at a rate of 50A/kg (0th to 20th cycle)
cycle) of the same nitrogen doped V2C>5-NiO-LiB02 glass composite material.

From Figure 15.1 the following features can be deduced: OCV = 3.16 V, cycling 4.5 - 1.5 V, ~ 77 Ah/kg capacity on the 1st charge to 4.5 V proving the chemical lithiation achieved by the reaction with Li3N. The first discharge capacity was ~ 362 Ah/kg. Then further cycling between 1.5 - 4.5 V was performed. At 8th cycle the charge capacity was ~ 378 Ah/kg and the discharge capacity ~ 375 Ah/kg.

From Figure 15.2 the following features can be deduced: OCV = 3.16 V, the first discharge capacity was ~ 291 Ah/kg. Then cycling was performed between 1.5 - 4.0 V. At the 20th cycle the charge capacity was ~ 277 Ah/kg and the discharge capacity ~ 275 Ah/kg.

Comparison with different systems:

Figure 16 shows a specific energy vs. cycle number plot for different materials of the present invention cycled between 1.5 V - 4.0 V at 50 A/kg. For the nitrogen doped V2C>5-NiO-LiB02 glass composite material, high specific energy was obtained with polarization at 10th cycle ~ 800 Wh/kg for charge and ~ 675 Wh/kg for discharge and the average voltage was about 2.4 V. For non N-doped V2C>5-NiO-LiB02 glass composite material, these values were ~ 1005 Wh/kg for charge and ~ 885 Wh/kg for discharge and the average voltage was about 2.4 V, so that there was a decrease in the specific capacity for the nitrogen doped sample. The values were 736 Wh/kg and 2.24V for redGO comprising V2C>5-LiB02 glass, and ~ 647 Wh/kg and 2.23V for plain V2C>5-LiB02 glass.

Advantages of the glassy composite materials of the present invention:

The inventive materials, wherein Li/NaBC>2 acts as the glass former and T_{x}O_{y}, in particular V2O5 as the main electrochemically active part and that have high
specific capacity and energy are suitable electronically active materials for Li-ion batteries. One of their advantages is that the synthesis method is very simple and cost efficient. Comparable cathode materials delivering close capacities and energies are only obtainable by laborious synthetic methods and using expensive techniques and educts. The specific advantages of important embodiments of the invention can be described as follows:

V2O5-L1BO2 glass:
The completely glassy material is obtained with only 20 wt-% L1BO2 meaning that the major part of the glass still is electrochemically active. Irreversible capacity loss that occurs for 3 lithium insertion in crystalline V2O5 phases is not found in this glass as the system cycles as a solid solution and there is no phase transformation in the first discharge.

V2O5-L1BO2 glass - reduced graphite oxide (redGO) composite:
The cycling properties and charge/discharge capacities of the V2O5-L1BO2 glass is improved by a better conducting carbon network obtained via reduction of well distributed graphite oxide. Besides, excess Li in the initial glass could be partially extracted in the first charge, which was not possible using plain V2O5-L1BO2 glass where Li remained therein as "dead weight".

V2C>5-NiO-LiB02 glass - reduced graphite oxide (redGO) composite:
NiO addition into the system increased the voltage range and so the specific energy of the system. In addition, the cycling in the broader voltage range, 4.5V-1.5V was advanced compared to the plain system (V2°5-L1BO2 glass). Though it was not tested, the thermal stability of the system is also thought to be improved.
N-doped V2C>5-NiO-LiB02 glass - reduced graphite oxide (redGO) composite:

The cycling stability and the columbic efficiency (when cycled between 1.5-4.0 V) were increased by nitrogen doping via the reaction with Li3N. In addition, the glass can be lithiated by this method, which is advantageous or even necessary for the commercial use if the anode part of the battery is chosen from a non lithiated material, such as graphite.

In order to specifically examine the features of the glassy material, the glass particles examined above were not provided with a coating. However, using special coatings on the surface of the glass particles, such as C, ZrC>2, Al2O3, Li3PO4, LiFePC>4, Li3B03 etc. is within the scope of the present invention. Such coatings may e.g. further improve stability since a main reason for stability problems is assumed to be the dissolution of the transition metal centers into the electrolyte.

Further improvement is obtainable through optimization of the particle sizes of the inventive glasses, since those examined above were still in the µm range. Big particle size of materials with low ionic conductivity is assumed to be the main reason for the large hysteresis of approx. 100-150 Wh/kg, observed.

While there are shown and described presently preferred embodiments of the invention, it is to be distinctly understood that the invention is not limited thereto but may be otherwise variously embodied and practiced within the scope of the following claims.
References


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Claims

1. A glass having the composition \((T_xO_y)z - M_uO_v)w - (Na/LiBC>2)t\) wherein
   \(T\) is a transition metal selected from \(V\) and \(Mo\),
   \(M\) is a metal selected from \(Ni, Co, Na, Al, Mn, Cr, Cu, Fe, Ti\) and mixtures thereof,
   \(x, y, u, \) and \(v\) are the stoichiometric coefficients resulting in a neutral compound, i.e. \(x = 2y/\text{(oxidation state of } T)\) and \(u = 2v/\text{(oxidation state of } M)\),
   \(z, w\) and \(t\) are weight-%, wherein
   \(z\) is 70-80,
   \(w\) is 0-20
   \(t\) is 10-30, and
   the sum of \(z, w\) and \(t\) is 100 weight-%.

2. The glass of claim 1 wherein \(T_xO_y\) is \(V_2O_5\).

3. The glass of claim 1 or 2 wherein \(w\) is 0.

4. The glass of any of the preceding claims wherein \(z\) is about 80, \(w\) is about 0 and \(t\) is about 20.

5. The glass of claim 1 or 2 wherein \(w\) is at least 1, preferably about 5.

6. The glass of claim 5 wherein \(z\) is about 80, \(w\) is about 5 and \(t\) is about 15.

7. The glass of any of the preceding claims wherein \(M_uO_v\) is selected from the group consisting of \(NiO, Co3O4, Na2O, Al2O3, MnO, MnC>2, CrC>3, CuO, Ni2O3, Fe2C>3, TiC>2\), and mixtures thereof.
8. The glass of any of the preceding claims wherein $M_0O_v$ is NiO.

9. The glass of any of claims 1 to 7 wherein $M_0O_v$ is Na20 and/or Al2O3.

10. The glass of any of the preceding claims that is enriched with Li due to doping with Li$_3$N.

11. A cathode material (composite) comprising a glass of any of the preceding claims together with carbon and/or graphite, in particular carbon and/or graphite obtained by reduction of graphite oxide, and optionally a binder.

12. A method for producing a glass of any of claims 1 to 10 comprising providing a composition by mixing, optionally and preferably with grinding, of $z$ wt-% of $T_xO_y$ and $w$ wt-% $M_0O_v$ and $t$ wt-% Na/LiBC>2 and heating the mixture to a temperature where a melt is formed but preferably not over 900°C, or not over 800°C for paramagnetic particles forming compositions, for a time sufficient to form a homogeneous melt, such as for 1 hour, followed by fast cooling (guenching).

13. A cathode comprising the glass of one of claims 1 to 10 or the cathode material of claim 11 on a current collector.

14. A rechargeable battery comprising a cathode of claim 13, an anode, a diaphragm and an electrolyte.
Fig. 3

Specific charge (Ah/kg)

Potential vs. L+I/L (volts)

(153)Y2O5 glass galvano 50
Fig. 5
Fig. 16
A. CLASSIFICATION OF SUBJECT MATTER

INV. C03C3/14  C03C3/145  C03C21/00  H01M4/131  H01M4/58

ADD.
According to International Patent Classification (IPC) and/or both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C03C  H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Date of the actual completion of the international search

11 June 2013

Date of mailing of the international search report

20/06/2013

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Heer, Stephan

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