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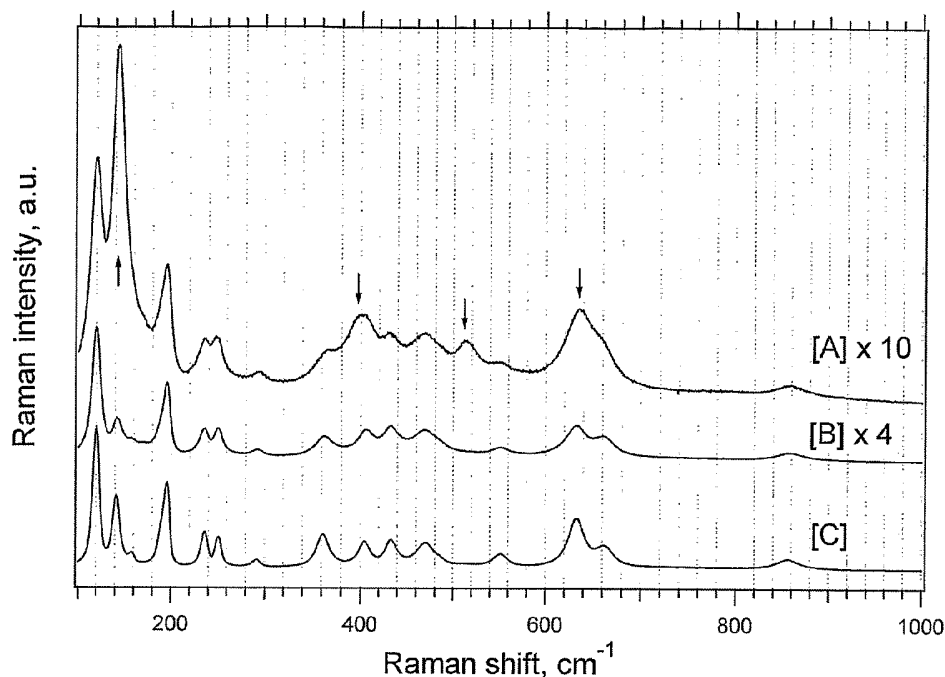
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(54) Title: ENERGY STORAGE DEVICE



(57) Abstract: High-energy and high power-density pseudocapacitive energy storage device is based on transition metal oxides having solid host structure with open parallel channels accessible to electrolyte ions. Examples of such structures are $\text{TiO}_2(\text{B})$, $\text{VO}_2(\text{B})$, FeV_3O_8 and AlNbO_4 . The energy storage is achieved by a pseudocapacitive process, which is not controlled by the diffusion of Li in the solid. The same material/process can be also used for hydrogen storage.



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Energy storage device

Field of the invention

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The invention relates to an energy storage device comprising a positive electrode, a negative electrode and an electrolyte. At least one electrode being made of metal oxide.

10 State of the art

The current Li-ion batteries are based on Li-insertion or Li-intercalation into suitable host structures, such as graphite or solid transition metal oxides ¹. The basic unit of a battery is an electrochemical cell with a positive electrode, a negative electrode and an electrolyte, the whole contained within a casing. Other components such as separators or gasket are also included. The charging/discharging rate is controlled by the diffusion of Li⁺ ions into/from the crystal lattice of the host. An alternative to the bulk charge accommodation is the surface charge storage in a supercapacitor, and there are also hybrid devices, in which one electrode works as the bulk charge storage medium (Li₄Ti₅O₁₂ spinel) and the second electrode as the surface charge storage medium (active carbon) ².

TiO₂(B) is a metastable monoclinic modification of titanium dioxide. It was first synthesized in 1980 by Marchand et al. ^{3,4} from a layered titanate K₂Ti₄O₉ by K⁺/H⁺ ion exchange followed by calcination. TiO₂(B) ⁵⁻⁸ and “monoclinic TiO₂” (apparently TiO₂(B)) ⁹ were traced during the synthesis of titania nanotubes by hydrothermal treatment of TiO₂ in NaOH medium. By tuning of the temperature and concentration of NaOH, either titanate nanotubes or TiO₂(B) nanowires were synthesized selectively ⁸. The structure of hydrothermally grown nanotubes has been a subject of considerable confusion in the past, but recent studies point at the layered titanate, H₂Ti₃O₇ as the main constituent of these nanotubes ^{7,8}. An alternative suggestion was that the hydrothermally grown titanate nanotubes are composed of orthorhombic lepidocrocite-like species,

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$H_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$ ($x \approx 0.7$, $\square$ = vacancy)¹⁰, which transforms directly to anatase by heating^{10,11}. However, this work was criticized by others⁷, and the sole presence of monoclinic titanates (tritanates) seems to explain the hydrothermal synthesis of nanotubes satisfactorily^{7,12}. Since the $H_2Ti_3O_7$ can be thermally dehydrated to $TiO_2(B)$
5 ^{7,13,14}, the existence of $TiO_2(B)$ nanotubes is supported, too⁷.

$TiO_2(B)$ was even found in nature by Banfield et al.¹⁵. Its crystal structure was first determined by Marchand et al.³. The structure was further refined by theoretical methods¹⁶, by X-ray¹³ and neutron diffraction¹⁴. $TiO_2(B)$ has monoclinic unit cell
10 (space group C2/m) with $a = 1.21787$ nm, $b = 0.37412$ nm, $c = 0.65249$ nm, $\beta = 107.054^\circ$ ¹⁴. The structure is isotypic to that of Na_xTiO_2 (bronze), $x \approx 0.2$, where the name “ $TiO_2(B)$ ” comes from. The same crystal structure is also represented by the mineral $Na_2Fe_2Ti_6O_{16}$ (freudenbergite)¹⁷. Hence, $TiO_2(B)$ can equally be called “freudenbergite modification of TiO_2 ”, but this name is not common. The density of $TiO_2(B)$ is 3.64-
15 3.76 g/cm³,^{4,15,18} i.e. it is smaller than that of anatase, rutile or brookite.

The electronic structure of $TiO_2(B)$ was calculated by Nuspl et al.¹⁹. $TiO_2(B)$ is n-type semiconductor with a band gap of 3 - 3.22 eV^{20,21}, which is similar to that of rutile and anatase. Due to its open structure, $TiO_2(B)$ accommodate hydrogen via electrochemical
20 reduction of inserted protons, and this hydrogen can be extracted photoelectrochemically in visible light²¹.

$TiO_2(B)$ accommodates Li^+ to form $Li_xTiO_2(B)$. This application is claimed in French Patent Application FR 2 482 787. The insertion coefficient x was found 0.75-0.85 by the
25 reaction with n-butyl-lithium and $x \approx 0.5 - 0.75$ by electrochemistry^{4,22-25}. The electrochemical reversibility of lithium insertion was, reportedly, not very good⁴. Recently, high electrochemical capacity ($x = 0.82$, i.e. 275 mAh/g) was reported for hydrothermally grown $TiO_2(B)$ nanowires, which were superior to the bulk $TiO_2(B)$ ⁸. A comparative theoretical study of Li-insertion into anatase and $TiO_2(B)$ points at beneficial
30 properties of the latter¹⁹. The $TiO_2(B)$ lattice has parallel infinite channels, in which Li^+ can be accommodated, without any significant distortion of the structure¹⁹.

The diffusion control of Li^+ storage in a bulk crystal can be traced by methods, such as cyclic voltammetry³³ and chronoamperometry³⁴, which employ concepts and principles translated, essentially, from the solution electrochemistry. This philosophy provides
5 useful physical parameters, such as diffusion coefficients of Li^+ in a solid. For instance, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (spinel)³⁵ and TiO_2 (anatase)^{33,34} have been successfully treated by this methodology.

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Summary of the invention

Electrochemical capacitors can be divided into two subcategories: (i) double-layer capacitors in which the interfacial capacitance at the electrode/electrolyte interface can be
15 modelled as two parallel sheets of charge; and (ii)

The present invention relates to certain solid host structures that could accumulate Li in a process, which is not controlled by the diffusion inside the solid, but the material behaves like a pseudocapacitive charge-storage medium. In a pseudocapacitor charge transfer between the electrolyte and the electrode occurs over a wide potential range as a result of
20 oxidation/reduction reactions between the electrode and the electrolyte. Pseudocapacitors are being developed for high-pulse power applications.

The inventors of the present patent application have surprisingly discovered that this pseudocapacitive energy storage can accumulate Li much faster than the process of ordinary lithium insertion or intercalation. Consequently, the power density of such
25 device is much higher. Compared to double-layer capacitive energy storage, our invention provides much higher energy density. A consequent requirement of any electrochemical cell is that it should have both high power and high energy densities. In the state of the art batteries, only one of these requirements has been achieved at reasonable cost, but not both.

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Thus, the present invention provides an electrochemical cell which may be used in a portable electronic devices, EV or HEV, while at least one of the electrodes comprise a solid host structure, which is not limited kinetically by the diffusion of Li inside the solid. An example of such electrode materials is $\text{TiO}_2(\text{B})$.

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EXPERIMENTAL SECTION

10 Materials

The precursor, X-ray amorphous TiO_2 , was prepared by precipitation of the aqueous solution of K_2TiF_6 (Aldrich) with ammonium hydroxide solution (25wt.%, Fluka). The product was washed with H_2O and dried, $S_{\text{BET}} = 584 \text{ m}^2/\text{g}$. The concentration of K was negligible in the product, as indicated by ESCA and AAS analyses. Alternatively, the amorphous TiO_2 ($S_{\text{BET}} = 518 \text{ m}^2/\text{g}$) was prepared by hydrolysis of titanium ethoxide at 0°C as described elsewhere³¹.

Sample A: 3.5g of amorphous TiO_2 was autoclaved in 100 mL of 10 M NaOH at 250°C for 48 hours, then washed with H_2O and autoclaved in 0.1 M HNO_3 at 200°C for 2.5 hours. The dried sample was then calcined at 500°C for 1 hour.

Sample B: 10 g of amorphous TiO_2 was mixed with 7.78 g of Cs_2CO_3 (Aldrich) and mortared carefully. The mixture was then decarbonated at 800°C for 4 hours, mortared again and annealed at 800°C in a crucible with a tight for 24 hours twice, with grinding at the interval. The product was then mortared and ion-exchanged with 1 N HCl for 4 x 24 hours at vigorous stirring with the fresh acid every 24 hours. The amount of 1N HCl was 100 mL per 1 g of product. The dried sample was finally calcined at 500°C for 1 hour. The product's surface area was $S_{\text{BET}} = 34.6 \text{ m}^2/\text{g}$.

Sample C: This material was prepared according to the original synthetic protocol of $\text{TiO}_2(\text{B})$ ³. An intimate mixture of 20 g KNO_3 (Aldrich) and 31.6 g of TiO_2 (Bayer, PKP04090) was annealed at 1000°C for 2 days. The product was mortared and

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hydrolyzed with 0.4 N HNO₃ for 3 days at vigorous stirring with the fresh acid every 24 hours. 1 g of the powder corresponded to 100 mL of 0.4 N HNO₃. The sample was dried in air at ambient temperature, then under vacuum overnight and calcined at 500°C for 30 min. The product's surface area was $S_{\text{BET}} = 9.7 \text{ m}^2/\text{g}$.

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Preparation of electrodes

Powder sample was dispersed in aqueous medium into viscous paste according to the previously developed methods^{28,32}. The powder (0.3 g) was mixed under stirring or
10 gentle mortaring with 0.8 mL of 10 % aqueous solution of acetylacetone. Subsequently, 0.8 mL of 4 % aqueous solution of hydroxypropylcellulose (Aldrich, MW 100,000) was added and finally 0.4 mL of 10 % aqueous solution of Triton-X100 (Fluka). Before use, the prepared slurry was homogenized by stirring. If the slurry was too viscous, it was further diluted by water. Titanium grid (5 x 15 mm, Goodfellow) was used as the
15 electrode support. Electrodes were prepared by dip-coating, the coated area was ca. 5 x 5 mm. The prepared electrodes were dried in air, and finally calcined in air at 450 °C for 30 min. The amount of active electrode material was between 0.2 to 0.7 mg. Blank experiments confirmed that a bare Ti grid had negligible electrochemical charge capacity compared to that of the active material. Alternatively, the slurry was also deposited on a
20 sheet of conducting glass (F-doped SnO₂, TEC 8 from Libbey-Owens-Ford, 8 Ω/square) using a doctor-blading technique³². The sheet of conducting glass had dimensions: 3 x 5 x 0.3 cm³. A Scotch-tape at both edges of the support (0.5 cm) defined the film thickness and left part of the support uncovered for electrical contact. The film was finally calcined for 30 min in air at 450°C. After cooling down to room temperature, the sheet was cut
25 into ten electrodes 1.5 x 1 cm² in size; the geometric area of the TiO₂ film was 1 x 1 cm².

Methods

Electrochemical measurements were carried out in an one-compartment cell using an
30 Autolab Pgstat-30 (Ecochemie) controlled by the GPES-4 software. The reference and auxiliary electrodes were from Li metal, hence, potentials are referred to the Li/Li⁺ (1M)

reference electrode. $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (Fluorad HQ 115 from 3M) was dried at 130°C/1 mPa. Ethylene carbonate (EC) and 1,2-dimethoxyethane (DME) were dried over the 4A molecular sieve (Union Carbide). The electrolyte solution, 1 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ + EC/DME (1/1 by volume) contained 15-40 ppm H_2O as determined by Karl Fischer
5 titration (Metrohm 684 coulometer). All operations were carried out under argon in a glove box. Raman spectra were excited by an Ar^+ laser at 2.41 eV (Innova 305, Coherent) and recorded on a T-64000 spectrometer (Instruments, SA).

10 RESULTS AND DISCUSSION

Fig. 1 shows Raman spectra of the prepared materials. Sample A is apparently a mixture of anatase and $\text{TiO}_2(\text{B})$, but the spectra of samples B and C can be assigned to pure $\text{TiO}_2(\text{B})$ ^{8,13,14}. The formation of pure $\text{TiO}_2(\text{B})$ in sample B (Fig. 1) is surprising. The
15 employed synthetic protocol should, actually, lead to the orthorhombic lepidocrocite-like protonic titanate, $\text{H}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4$. This species is characterized by ideally flat sheets of edge-sharing TiO_6 octahedra ³⁶⁻³⁸, which should convert directly into anatase ^{10,11}, without the intermediate crystallization of $\text{TiO}_2(\text{B})$. Commercial nanocrystalline anatase TiO_2 (Bayer) provided mixtures of $\text{TiO}_2(\text{B})$ and anatase or pure anatase in the final product,
20 but the synthesis starting from amorphous TiO_2 (see Experimental Section) lead, unexpectedly, to pure $\text{TiO}_2(\text{B})$.

Fig. 2 shows cyclic voltammograms of samples A and B. The voltammogram of sample A exhibits a pair of cathodic/anodic peaks at 1.75 & 1.95 V (formal potential 1.85 V),
25 which are characteristic for Li-insertion into anatase lattice ^{28,29,32,33,39-43}. We have previously denoted this pair of peaks as “A-peaks” ²⁸. In addition to that, the voltammogram shows two pairs of peaks with formal potentials of 1.52 and 1.59 V vs. Li/Li^+ , respectively, denoted S1 and S2, respectively ²⁸. The notation came from our assumption that these S-peaks could be assigned to the surface-confined process in titania
30 nanosheets ²⁸ or in “amorphous phase” ^{26,27}. However, this assumption needs revision in view of the new facts accumulated here.

The sole features assignable to S-peaks occur in both samples B and C, which are pure TiO₂(B). This generates a logical conclusion that the S-peaks at 1.52 and 1.59 V are, actually, signatures of TiO₂(B). The Li-storage capacity (Li/Ti = x) at the slowest voltammetric scan (0.1 mV/s) was 0.53 (sample A), 0.68 (sample B). These capacities are comparable to those reported for galvanostatic charging of bulk TiO₂(B) ($x \approx 0.5$ -0.75)^{4,22-25} but smaller than the values obtained for galvanostatic charging of TiO₂(B) nanowires ($x = 0.82$)⁸. Also from theoretical arguments, the Li-insertion beyond the $x = 0.5$ becomes rather difficult¹⁹.

Fig. 3 demonstrates the behavior of S-peaks in phase-pure sample B at varying scan rates. The peak currents were normalized with respect to the peak current at the slowest scan (0.1 mV/s) and plotted against the scan rate (inset in Fig. 3). Apparently, the currents scale with the first power of scan rate, which is typical for capacitive charging:

$$i = dQ/dt = C dE/dt = Cv, \quad (1)$$

Q is the voltammetric charge and dE/dt the scan rate, v . However, sole capacitive double-layer charging (Eq. 1) should give featureless voltammogram (ideally rectangle assuming C invariant of potential). The peak structure with small peak-to-peak splitting (ca. 50-100 mV at $v = 0.1$ mV/s) points at a surface-confined charge transfer process, which can be considered faradaic pseudocapacitance. The found Li-storage capacity ($x \approx 0.5$ -0.7) considerably exceed the "ordinary" capacity of the TiO₂ surface assuming solely the double-layer plus the faradaic pseudocapacitance of surface states³⁹. Consequently, this behavior is specific for the TiO₂(B), and we may suggest that its open structure with freely accessible channels¹⁹ is responsible for this unusually fast Li-charging of a TiO₂(B) crystal.

The different mechanism of Li-storage in TiO₂(B) and anatase is explicitly demonstrated on sample A (Fig. 4) which is a mixture of both phases. The plot of peak currents against the scan rate is shown on chart B (Fig. 4). In order to analyze this dependence in broader

interval of ν , we selected here the cathodic S-peaks and anodic A-peaks, which are better resolved at faster charging (cf. also Fig. 3). (However, the conclusions are generally valid for both cathodic and anodic peaks). Apparently, the A-peaks scale with square root of the scan rate, ν , as it is expected for diffusion controlled irreversible kinetics^{33,43}:

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$$|i| = 0.4958nFAc(D\alpha nF\nu/RT)^{1/2} \quad (2)$$

where n is number of electrons, A is the electrode area, c is the maximum concentration of Li^+ (or Ti^{3+}) in the accumulation layer ($c = 0.024 \text{ mol/cm}^3$ for $x = 0.5$; cf. Eq. 1), D is diffusion coefficient and the other symbols have their usual meaning. Fig. 4B confirms that this dependence can be fitted to experimental points for $\nu < \approx 2 \text{ mV/s}$. (For higher scan rates, the fit is still good, but the experimental points show systematic negative deviation, due to uncompensated iR drop of the cell). The behavior described by Eq. 2 is typical for Li-insertion into "ordinary" anatase lattice^{26-29,32,33,39-42}. The $i \approx \nu^{1/2}$ dependence was even found for Li-insertion into titania nanosheets derived from lepidocrocite-like titanate⁴⁴.

Li-insertion into pure $\text{TiO}_2(\text{B})$ was previously studied mostly by galvanostatic chronopotentiometry^{8,22,24}. This technique is less suitable for the detection and analysis of the S-peaks. However, by derivatization of the chronopotentiometric curve and plotting of dx/dE vs. E , two pairs of cathodic/anodic peaks at ca. 1.5 and 1.6 V can be traced²⁴. Zachau-Christiansen et al.²⁴ have suggested that these peaks indicate two ordered superstructures with $x = 0.33$ and $x = 0.5$. Such peaks are virtually identical to our S-peaks. Also we may note that the S-peak at 1.6 V is stronger than the S-peak at 1.5 V (Fig. 2), i.e. the first formed superstructure (at 1.6 V) is slightly more populated by Li than the superstructure formed at 1.5 V. However, none of the previous electrochemical studies on $\text{TiO}_2(\text{B})$ ^{4,5,8,19,22,24,25} mentioned the pseudocapacitive nature of charging.

The fact that Li is accommodated in $\text{TiO}_2(\text{B})$ via pseudocapacitive process recalls the idea of fast transport of Li^+ in parallel channels of $\text{TiO}_2(\text{B})$ lattice¹⁹. Li^+ can be very mobile inside these channels by easy hopping between occupied and unoccupied sites¹⁹.

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All these channels are structurally equivalent, and also the structure of $\text{Li}_{0.5}\text{TiO}_2(\text{B})$ is assumed to have only crystallographically equivalent sites occupied by Li^+ ¹⁹. Nevertheless, there are further vacant sites up to the stoichiometry of $\text{LiTiO}_2(\text{B})$ ¹⁹. All these sites are pseudo-octahedral with a coordination number 5 (LiO_5) ^{19,25}, while two
5 kinds of these sites are detectable by ^7Li -NMR ²⁵.

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Figure captions

10 **Figure 1:** Raman spectra of the prepared materials [A] Sample prepared by hydrothermal growth [B] sample prepared from amorphous TiO_2 [C] sample prepared from $\text{H}_2\text{Ti}_4\text{O}_9 \cdot \text{H}_2\text{O}$ (bronze). Spectra B and C are assignable to monoclinic $\text{TiO}_2(\text{B})$, spectrum [A] shows also the anatase peaks (marked by arrows) in addition to $\text{TiO}_2(\text{B})$. The Raman intensities of samples A and B are multiplied by a factor of 10 and 4, respectively.
15 Spectra are offset for clarity.

Figure 2: Cyclic voltammograms in 1M $\text{LiN}(\text{CF}_3\text{SO}_2)_2 + \text{EC/DME}$ (1:1, v:v); scan rate 0.1 mV/s. [A] Sample prepared by hydrothermal growth [B] sample prepared from from amorphous TiO_2 .

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Figure 3: Cyclic voltammograms of sample B in 1M $\text{LiN}(\text{CF}_3\text{SO}_2)_2 + \text{EC/DME}$ (1:1, v:v); scan rate 0.1 – 1.2 mV/s (in 0.1 mV/s steps for plots from bottom to top). Inset displays the normalized peak current, i/i_{01} , where i_{01} is the peak current at the slowest scan (0.1 mV/s).

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Figure 4: Cyclic voltammograms of sample A in 1M $\text{LiN}(\text{CF}_3\text{SO}_2)_2 + \text{EC/DME}$ (1:1, v:v); scan rate 0.1 – 1.0 mV/s (in 0.1 mV/s steps for plots from bottom to top). Inset displays the absolute values of normalized peak current, i/i_{01} , where i_{01} is the peak current at the slowest scan (0.1 mV/s). Circles: anodic peak at ca. 2 V; crosses: cathodic peak at
30 ca. 1.5 V, squares: cathodic peak at ca. 1.6 V.

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Claims

1. Electrochemical cell comprising at least one electrode made of a metal oxide suitable for Li accommodation via a pseudocapacitive process.
- 5 2. Electrochemical cell according to claim 1 having a power density higher than commercial Li-ion batteries, utilizing Li-accommodation via a process controlled by the diffusion inside the solid, and the energy density higher than commercial supercapacitors where the charge storage occurs at the surface.
- 10 3. Electrochemical cell according to claim 1 or 2 comprising at least one electrode from a $\text{TiO}_2(\text{B})$, which is suitable for Li accommodation via a pseudocapacitive process.
- 15 4. Electrochemical cell according to claim 3, where $\text{TiO}_2(\text{B})$ is active material for the negative electrode.
5. Electrochemical cell according to claim 3, where the negative electrode is made from $\text{TiO}_2(\text{B})$ and is combined with positive electrode like LiCoO_2 ,
20 LiMn_2O_4 , LiFePO_4 , LiNiO_2 .
6. Electrochemical cell according to claim 3 having an energy density higher by a factor of 1.16 compared with similar cell using TiO_2 (anatase).
- 25 7. Electrochemical cell according to claim 3 having an energy density of at least 420 milliwatt-hour per gram (420mWh/g).
8. Electrochemical cell according to claim 3 having a peak power density higher by a factor of 2 compared with the cell using TiO_2 (anatase) at the scan rate of
30 2 mV/s.

9. Electrochemical cell according to claim 3 having a peak power density of at least 20 Watt per gram ($>20\text{W/g}$).
- 5 10. Hydrogen storage device comprising at least one electrode made of a metal oxide.
11. Hydrogen storage device according to claim 10 comprising at least one electrode made of $\text{TiO}_2(\text{B})$.
- 10 12. Pseudocapacitor comprising at least one electrode made of $\text{TiO}_2(\text{B})$.
13. Use of an electrode made of $\text{TiO}_2(\text{B})$ in a pseudocapacitor.
- 15 14. Electrochemical cell according to claim 1 having an electrode of metal oxide comprising current collector, binder and conducting additives.
15. Synthetic method providing phase-pure $\text{TiO}_2(\text{B})$ from amorphous TiO_2 and Cs_2CO_3 via solid state reaction, Cs^+/H^+ exchange and thermal dehydration.

Fig. 1

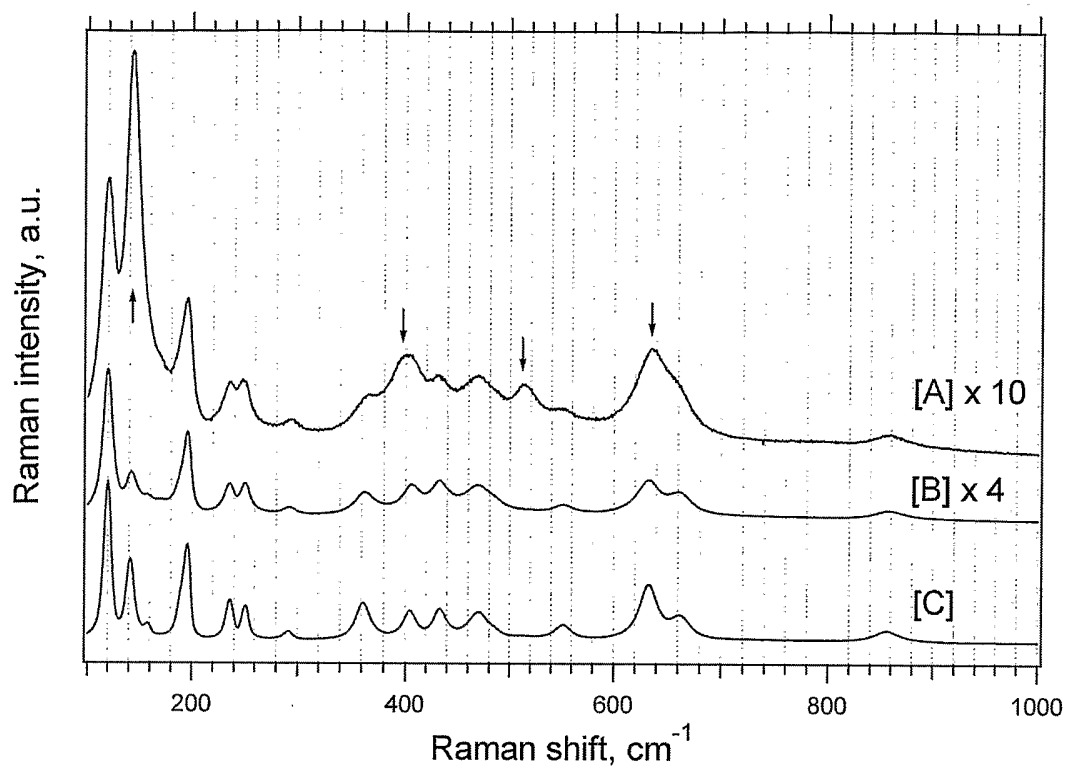


Fig. 2

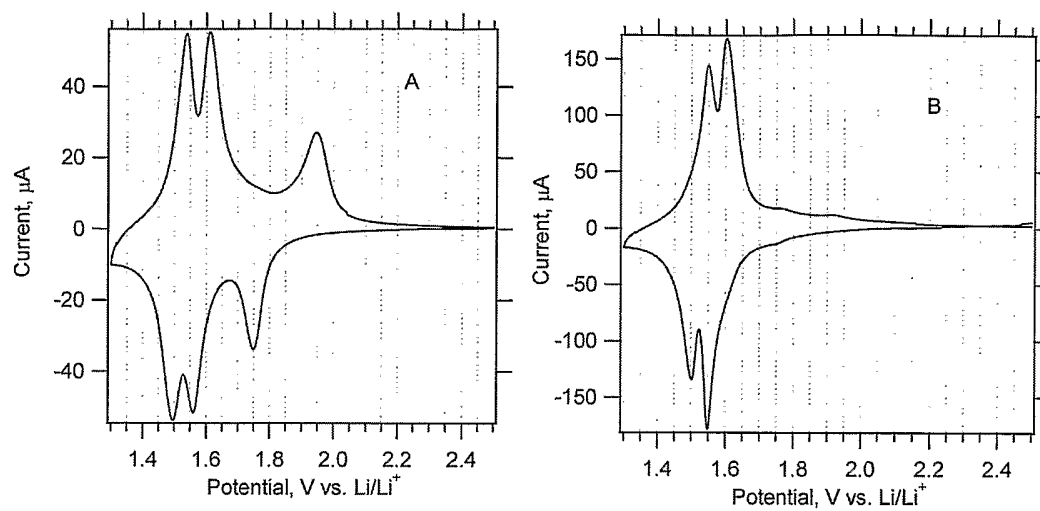


Fig. 3

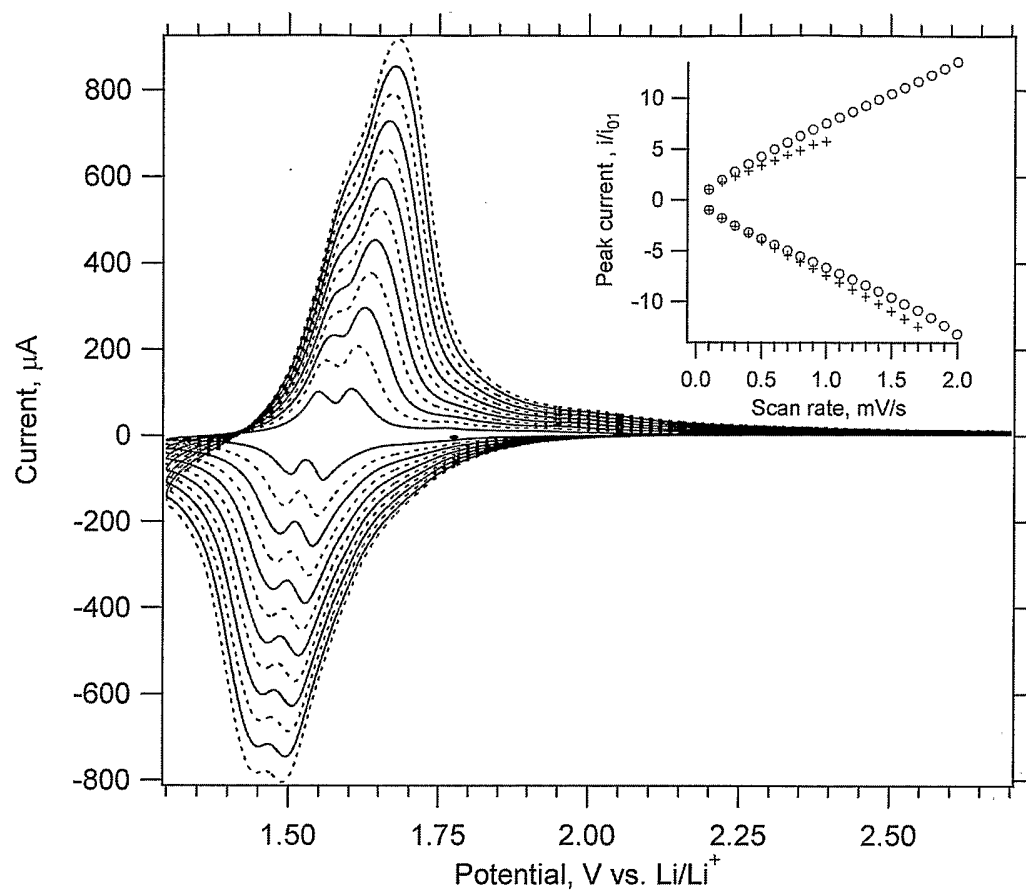


Fig. 4

