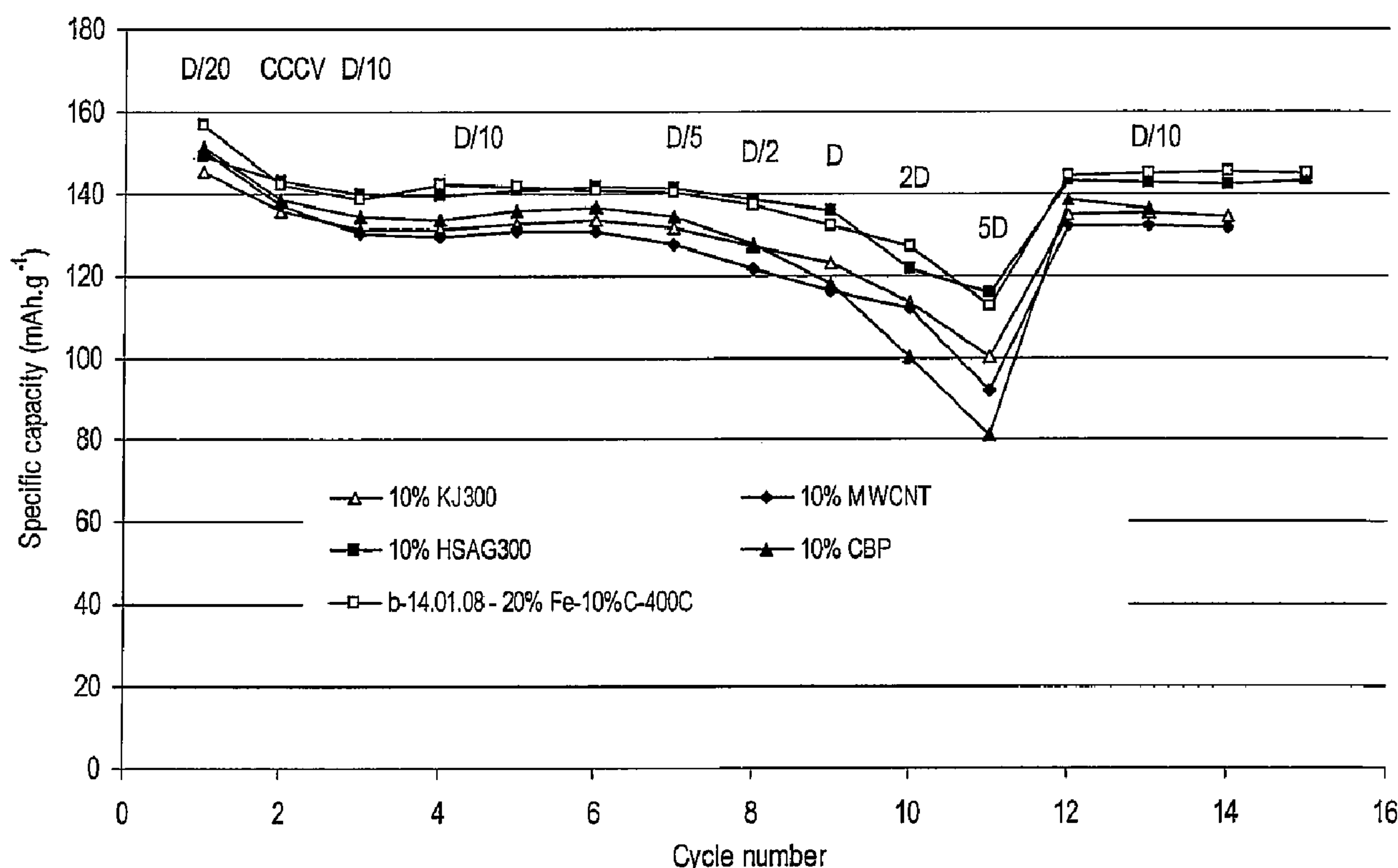




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(54) **Titre : NANOCOMPOSITES DE PHOSPHATE DE LITHIUM ET DE MANGANESE/CARBONE EN TANT QUE MATIERES ACTIVES DE CATHODE POUR DES BATTERIES AU LITHIUM SECONDAIRES**
(54) **Title: LITHIUM MANGANESE PHOSPHATE/CARBON NANOCOMPOSITES AS CATHODE ACTIVE MATERIALS FOR SECONDARY LITHIUM BATTERIES**



(57) **Abrégé/Abstract:**

The invention relates to a lithium manganese phosphate/carbon nanocomposite as cathode material for rechargeable electrochemical cells with the general formula $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z/\text{C}$ where M is at least one other metal such as Fe, Ni, Co, Cr, V, Mg, Ca, Al, B, Zn, Cu, Nb, Ti, Zr, La, Ce, Y, $x = 0.8-1.1$, $y = 0.5-1.0$, $0.9 < z < 1.1$, with a carbon content of 0.5 to 20% by weight, characterized by the fact that it is obtained by milling of suitable precursors of $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ with electro-conductive carbon

(57) Abrégé(suite)/Abstract(continued):

black having a specific surface area of at least 80 m²/g or with graphite having a specific surface area of at least 9.5 m²/g or with activated carbon having a specific surface area of at least 200 m²/g. The invention also concerns a process for manufacturing said nanocomposite.

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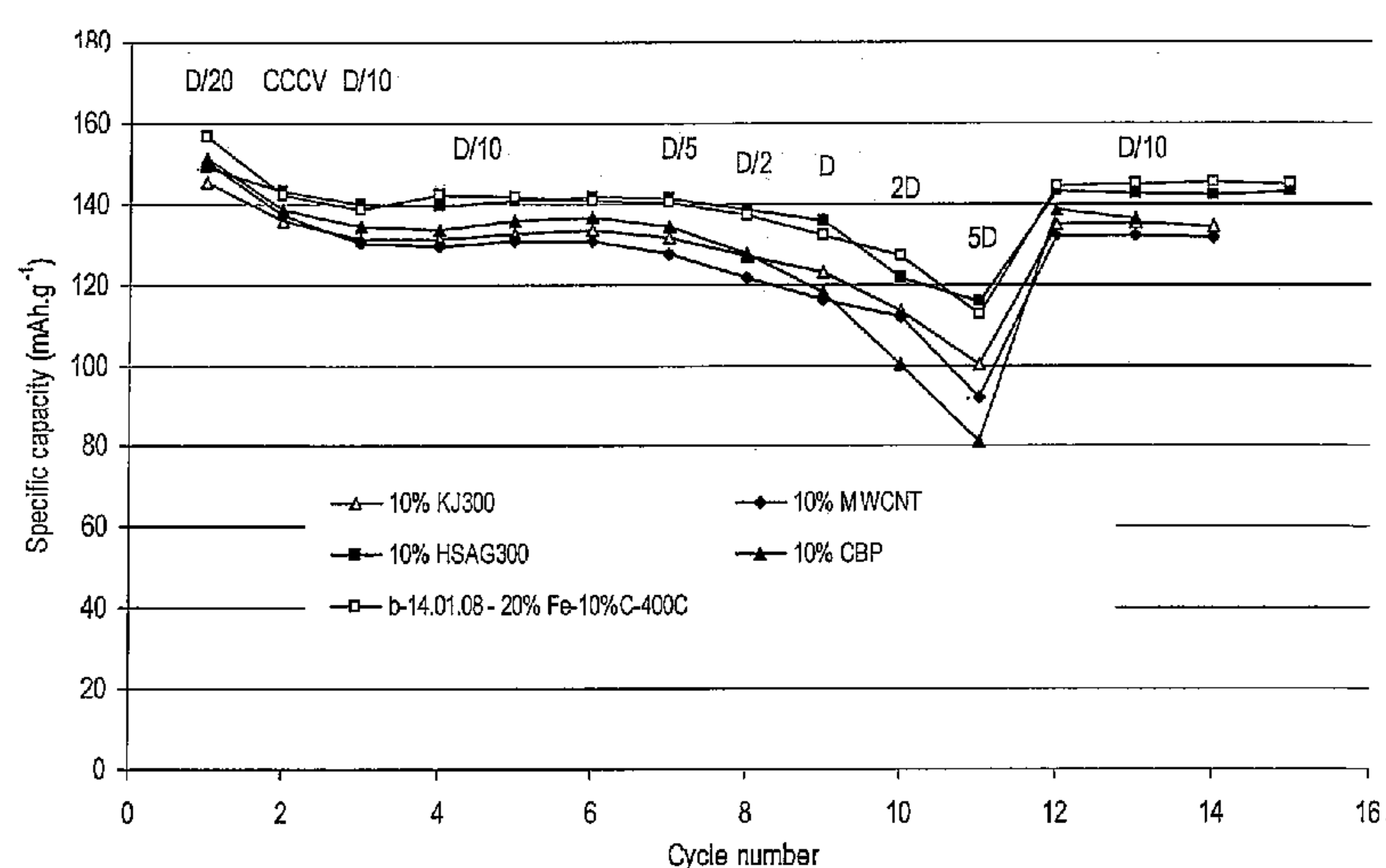


Figure 7

(57) **Abstract:** The invention relates to a lithium manganese phosphate/carbon nanocomposite as cathode material for rechargeable electrochemical cells with the general formula $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z/\text{C}$ where M is at least one other metal such as Fe, Ni, Co, Cr, V, Mg, Ca, Al, B, Zn, Cu, Nb, Ti, Zr, La, Ce, Y, $x = 0.8-1.1$, $y = 0.5-1.0$, $0.9 < z < 1.1$, with a carbon content of 0.5 to 20% by weight, characterized by the fact that it is obtained by milling of suitable precursors of $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ with electro-conductive carbon black having a specific surface area of at least $80 \text{ m}^2/\text{g}$ or with graphite having a specific surface area of at least $9.5 \text{ m}^2/\text{g}$ or with activated carbon having a specific surface area of at least $200 \text{ m}^2/\text{g}$. The invention also concerns a process for manufacturing said nanocomposite.

Lithium manganese phosphate/carbon nanocomposites as cathode active materials for secondary lithium batteries

5

FIELD OF THE INVENTION

10 The invention relates to a lithium manganese metal phosphate/carbon nanocomposite as cathode material for rechargeable electrochemical cells.

STATE OF THE ART

15

Rechargeable batteries of high energy density and long lifetime based on the reversible intercalation of lithium into certain materials have enabled the wide distribution of light and compact electronic devices, such as mobile phones and portable computers. However, the use of certain cathode materials, such as LiCoO_2 , has given rise to concerns because of the toxicity of cobalt and the danger of fire and explosion due to oxygen liberation and violent reaction with the organic electrolyte on overcharging or at elevated temperature (thermal runaway). Moreover cobalt is a rather rare and hence expensive element. Other materials, such as LiMn_2O_4 suffer from poor long term stability.

20

25 Lithium metal phosphates with olivine structure have emerged as a promising alternative as cathode materials, since the oxygen is strongly covalently bound in PO_4^{3-} , preventing the release of oxygen even under extreme conditions. In addition the inductive effect of PO_4^{3-} raises the redox potential of the metal centre, rendering the use of abundant and cheap metals such as iron and manganese possible. Thus, LiFePO_4 yields a voltage of 3.4 V against lithium and remains stable over thousands of charge/discharge cycles, even upon overcharge and at elevated temperature. LiMnPO_4 gives an even higher voltage of 4.1 V against lithium, which is near the stability limit of common non-aqueous electrolytes and more compatible with

30

classic systems, such as LiCoO_2 , $\text{LiAl}_{0.05}\text{Co}_{0.15}\text{Ni}_{0.8}\text{O}_2$ or LiMn_2O_4 . Thanks to the higher voltage LiMnPO_4 offers a superior energy density to LiFePO_4 , which is important for many applications, especially battery electric vehicles.¹ However, only solid solutions $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ were reported to be electrochemically active.²⁻⁴ Still, the capacity of $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ was limited to 80 mAh/g, which is less than half the theoretical capacity of 170 mAh/g.

Almost full capacity has been reported for LiMnPO_4 and $\text{Li}_{1-x}\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4$ prepared by ball milling of the precursors (MnCO_3 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$ and Li_2CO_3) with acetylene black and subsequent firing under inert gas atmosphere.⁵⁻¹⁶ It was claimed that this results in a grain size of $\text{Li}_{1-x}\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4$ not larger than 10 μm , with the BET specific surface area not being less than 0.5 m^2/g .^{5, 6, 8-10, 15} At a carbon content of 10% and a current density of 0.28 mA/cm^2 a capacity of 164 mAh/g was reported for a Mn content of $y = 0.75$.¹⁶ Unfortunately, neither the charge/discharge rate nor the loading of active electrode material were indicated by the authors, but assuming a typical loading of 34 mg/cm^2 cited in their patent application¹⁵ a current density of 0.28 mA/cm^2 corresponds to 8.2 mA/g, or a C-rate of C/20 (that is a charge/discharge time of 20 hours).

The poor electrochemical performance of LiMnPO_4 and $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ has been attributed to their extremely low electronic and ionic conductivities.^{17, 18} Many efforts have therefore been undertaken to reduce the particle size to the sub-micrometer scale and coat such nanoparticles with conducting carbon, in order to diminish electric and Li-diffusion resistances by shortening the distances for electron and lithium transport.

Direct precipitation of LiMnPO_4 from aqueous medium produced particles down to about 100 nm, which after ball-milling with acetylene black gave reversible capacities of about 70 mAh/g at C/20.^{17, 19, 20} Hydrothermal synthesis of LiMnPO_4 produced platelets of 100-200 nm thickness, which after ball-milling with carbon black yielded a reversible capacity of 68 mAh/g at a current density of 1.5 mA/g.²¹ Solid-state synthesis of $\text{LiMn}_{0.6}\text{Fe}_{0.4}$ by ball-milling followed by in situ carbon coating through pyrolysis of polypropylene produced 100-200 nm particles and an initial discharge capacity of 143 mAh/g at C/10.²² Sol-gel synthesis of LiMnPO_4 produced particles of 140-220 nm, which were reduced to 90-130 nm by ball-milling with acetylene black and yielded 134 mAh/g at C/10.²³⁻²⁵ Nanoparticles of LiMnPO_4 of 20-100 nm were obtained by a polyol process, which after ball-milling with acetylene

black gave a capacity of about 120 mAh/g at C/10.^{26, 27} In conclusion good rate performance, i.e. high capacity at higher C-rates has still not been reported.

Rate performance is essential for high power applications, such as electric vehicles. Various
5 physical parameters are expected to be responsible for poor kinetics and fast aging of Mn-rich
LMFP, including: the large lattice mismatch at the interface between lithiated and delithiated
phase; and the Jahn-Teller lattice distortion associated with Mn^{3+} .^{13, 28-33} Indeed, Kopeć et
al.³⁴ reported recently that the Mn^{3+} -ions in excess of a critical concentration of 60% undergo
transition to the low-spin state, which should renders delithiation (charging) very difficult. In
10 addition, first-principles calculations of the surface redox potentials of LMP indicate a large
difference between the Li redox potential in the (010) surface layers and the bulk, which
creates a high energy barrier for Li in the bulk to diffuse out of the particle, which, if correct
would render initiation and charging of the material impossible.³⁵

15 It has been demonstrated that the presence of a metal oxide interface layer between the
 LiMnPO_4 material, and the carbon layer improved electrochemical performance, and close to
theoretical capacity was observed at low rates.^{26, 27}

In specific, the presence of a manganese oxide interface layer between the LiMnPO_4 material,
and the carbon layer improved electrochemical performance. The metal oxide interface layer
20 between LiMnPO_4 and carbon can be detected by Raman spectroscopy. A 633 nm excitation
wavelength was used to observe the highest relative intensity of metal oxide bands compared
with phosphate bands. The close resemblance of its peak pattern to hausmannite is evident.^{26,}
²⁷ Lower symmetry and/or presence only in a thin layer on the LMP-carbon interface can be
also responsible for some peak broadening and downshifting compared to Hausmannite. The
25 sharpness of the Mn-O bands in LMP without Mn-oxalate even at lower laser power indicates
that this manganese oxide has not been generated by the laser-induced heating.

The manganese oxide layer is shown to be either Mn_3O_4 (hausmannite), $\beta\text{-MnO}_2$ (pyrolusite),
 MnO (manganosite), MnOOH (groutite) or $\text{Mn}_{1.85}\text{O}_{0.6}\text{H}_2\text{O}$ (birnessite).^{26, 27} The method to
prepare the manganese oxide interface layer required a ready-made LiMnPO_4 and milled
30 together with a carbon source.^{26, 27} In no cases were pre-cursors of LiMnPO_4 and carbon or a
pre-cursor of carbon were milled to form in-situ both the LiMnPO_4 and the manganese oxide
interface layer between the LiMnPO_4 material, and the carbon layer.

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According to the state of the art lithium metal phosphates LiMPO_4 should contain metals M and phosphate PO_4 in stoichiometric ratio $\text{M/PO}_4 = 1$ in order to form a pure single phase material. Any deviations from nominal stoichiometry generally result in the formation of undesirable impurity phases.

5 DESCRIPTION OF THE INVENTION

The invention relates to a new nanocomposite of lithium manganese phosphate, and a process for manufacturing such a nanocomposite.

In a claimed embodiment, the present invention relates to a lithium manganese phosphate/carbon nanocomposite suitable as a cathode material for rechargeable
 10 electrochemical cells, having the general formula $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z/\text{C}$ wherein: M is at least one other metal selected from the group consisting of Fe, Ni, Co, Cr, V, Mg, Ca, Al, B, Zn, Cu, Nb, Ti, Zr, La, Ce and Y; $x = 0.8-1.1$; $y = 0.5-1.0$; and $0.9 < z < 1.1$, with a carbon content of 0.5 to 20% by weight, obtained by heating and milling a precursor of $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ (lithium metal phosphate) with: (a) electro-conductive carbon black having a specific surface
 15 area of at least $80 \text{ m}^2/\text{g}$; (b) graphite having a specific surface area of at least $9.5 \text{ m}^2/\text{g}$; or (c) activated carbon having a specific surface area of at least $200 \text{ m}^2/\text{g}$.

In a claimed embodiment, the present invention relates to a process for the production of a lithium manganese phosphate/carbon nanocomposite as defined herein, comprising heating and milling the lithium metal phosphate precursor with: (a) electro-conductive carbon black
 20 having a specific surface area of at least $80 \text{ m}^2/\text{g}$; (b) graphite having a specific surface area of at least $9.5 \text{ m}^2/\text{g}$; or (c) activated carbon having a specific surface area of at least $200 \text{ m}^2/\text{g}$.

According to the present invention good capacity even at high C-rate is obtained with a nanocomposite of lithium manganese phosphate with general formula $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z/\text{C}$ where M is at least one other metal (e.g. Fe, Ni, Co, Cr, V, Mg, Ca, Al, B, Zn, Cu, Nb, Ti, Zr, La, Ce, Y) and $x = 0.8-1.1$ and $y = 0.5-1.0$ and $z = 0.9 < z < 1.1$ with a carbon content of 0.5
 25 to 20% by weight. Part of the oxygen atoms O may be substituted by fluorine F or part of the phosphate ions PO_4^{3-} may be substituted by silicate ions SiO_4^{4-} , sulfate ions SO_4^{2-} , vanadate ions VO_4^{3-} or borate ions BO_3^{3-} .

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The nanocomposite according to the invention is produced by milling of suitable precursors of $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ with electro-conductive carbon black having a specific surface area of at least $80 \text{ m}^2/\text{g}$, or with activated-carbon having a specific surface area of at least $200 \text{ m}^2/\text{g}$, or with graphite having a specific surface area of at least $9.5 \text{ m}^2/\text{g}$. The reactive milling can be
5 made under inert or reducing atmosphere or direct under air atmosphere, the rest of oxygen will be rapidly consumed by the carbon. To avoid oxidation of metals addition of antioxidant as vitamins C or a reducing agent can be applied.

Milling breaks covalent bonds in the carbon material and creates highly reactive coordinatively unsaturated carbon atoms (dangling bonds) on the carbon surface with which
10 said precursors can react. This mechanochemical reaction³⁶⁻³⁸ results in a nanocomposite of said precursors and carbon, wherein the size of the different domains can be controlled by the amount and type of carbon material as well as by the intensity and duration of milling. Thermal treatment leads to crystallization of $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ already at relatively low temperature due to intimate mixing of the precursors by milling. This low crystallization

temperature in combination with the covalently bound carbon prevents crystal growth and results in the small nanoparticle size of $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ in intimate contact with conducting carbon required for good rate performance.

5 Acetylene black has most often been used for the synthesis of LiMPO_4 / carbon composites by milling.^{5-9, 13-15, 39-43} Acetylene black has a BET specific surface area of only about 70 m^2/g . Like other conventional carbon blacks of modest specific surface area, including Vulcan XC 72R it consists of fused spherical primary particles (nodules) of about 10-50 nm diameter with onion-shell structure of concentric graphene like outer layers, while the core is more
10 amorphous.⁴⁴⁻⁴⁶ The compactness and resilience of these nodules renders them rather resistant against breakdown by milling (Figure 24 and 25). Therefore the carbon nodules mainly make point-contacts with the nanoparticles of the active material, which results in poor electrochemical performance (Fig. 8) due to the very low conductivity of $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$. This is different from the less insulating LiFePO_4 , where point-contacts between small
15 enough particles and carbon black have been reported to be sufficient for good performance.⁴⁷ This explains why acetylene black yields only poor rate performance (Figure 8).

Conductive carbon blacks with high specific surface area according to the present invention are for example the furnace blacks Printex® XE 2 (Evonik Degussa) with 950 m^2/g and fused
20 carbon nodules of about 30 nm diameter, as well as Black Pearls® 2000 (Cabot) with 1500 m^2/g and 15 nm particle diameter. The much higher specific surface area as compared to acetylene black in spite of the similar nodule size is due to a more open, porous structure of these nodules, rendering them much more fragile against milling. Therefore milling not only breaks the chains of fused carbon nodules but also disrupts the graphene like shells of the
25 nodules, creating dangling bonds for reaction with the $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ precursors.

Ketjenblack® (Akzo Nobel) is another conductive carbon black of high specific surface area (600-1400 m^2/g). It is obtained as by-product in the synthesis of ammonia and has a fused broken egg-shell structure, which arises from removal of the inner amorphous part of the
30 carbon black nodules by partial combustion.^{46, 48} These shells of about 20 nm outer diameters have a thickness of a few graphene layers only and thus are easily broken by milling, which results in a intimate large-area contact with the active material (Figure 23).

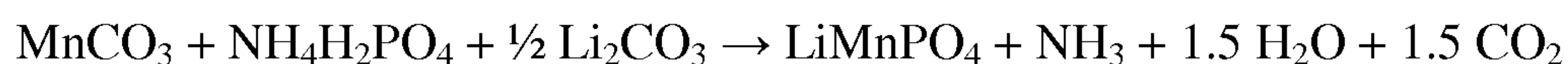
Activated carbons are another class of conductive carbon of high specific surface area (200-3000 m^2/g), examples include Norit® DLC Super 50. It is obtained via the reactive removal

of the inner amorphous part of the carbon by an activation process, creating a pore network. The fragile and brittle nature of the porous residual renders it easily broken by milling, the high surface area results in an intimate large-area contact with the active material.

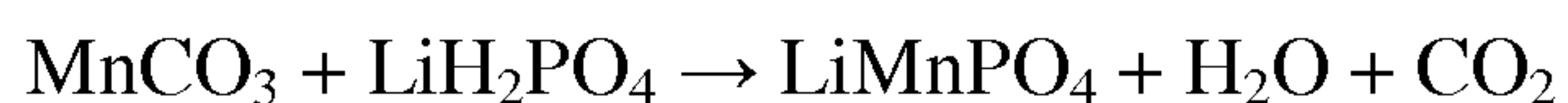
- 5 Graphitic nano-sheets can also be obtained by milling of graphite.⁴⁹⁻⁶⁰ Natural as well as synthetic graphite consists of stacked graphene sheets, which are bound by weak van der Waals forces only, and hence are easily separated by shear forces during milling. This produces thinner graphene stacks which are more easily broken within the graphene planes by further milling, creating highly reactive dangling bonds at the freshly created edges. The
- 10 milling time can be reduced by using expanded graphite, in which the graphene sheets have already been partially separated by chemical intercalation and thermal expansion. To reduce the milling time even further multiple or single sheet graphene can also be prepared by oxidation of graphite and subsequent exfoliation.⁶¹
- 15 Breaking of carbon-carbon bonds by milling creates highly reactive coordinatively unsaturated carbon atoms (dangling bonds).⁶²⁻⁶⁵ This freshly created carbon surface can react with the other precursors present in the mill.

For the solid state synthesis of LiMnPO_4 by mechanochemical reaction the use of

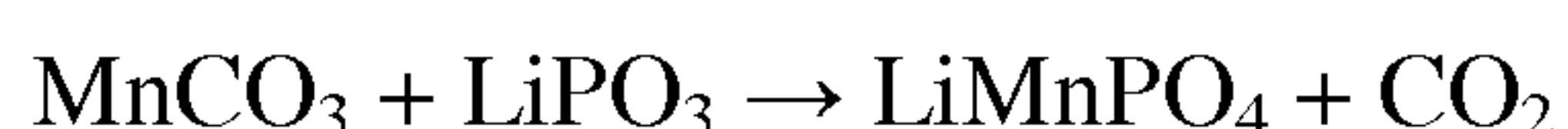
20 manganese(II)carbonate, ammonium di-hydrogen-phosphate and lithium carbonate has been reported:^{5-12, 16, 66}



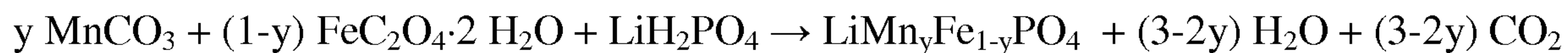
- 25 According to the present invention the liberation of toxic, corrosive and flammable NH_3 during milling can be avoided with lithium-di-hydrogen-phosphate:



- 30 This also reduces the amount of water and carbon dioxide produced by 50%. Water as byproduct may be avoided completely by employing lithium metaphosphate:



Solid solutions with lithium iron phosphate can be obtained with e.g. iron oxalate:



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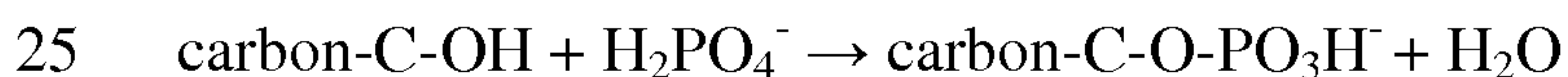
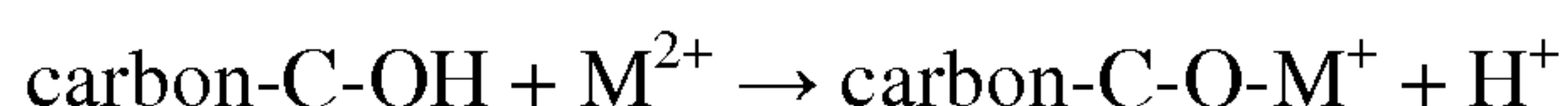
Other lithium metal phosphates and their solid solutions can be synthesized accordingly from the appropriate precursors. Instead of metal carbonates or oxalates any other suitable metal source can be used, such as oxides (e.g. MnO, Mn₂O₃, MnO₂, Fe₃O₄, Fe₂O₃), hydroxides, salts with carboxylic acids (e.g. acetates) or hydroxyl carboxylic acids (e.g. glycolates, lactates, citrates, tartrates). Other lithium salts can be employed instead of LiH₂PO₄ or LiPO₃, such as Li₂O, LiOH or Li₂CO₃. Phosphate ions can also be introduced from phosphoric acid (HPO₃ or H₃PO₄), as well as any phosphate salt, as long as the byproducts do not degrade the main product.

15 The water vapor produced by the mechanochemical reaction can dissociatively react with the freshly created carbon surface arising from disruption of carbon-carbon bonds by milling, resulting in a hydroxylation of the coordinatively unsaturated carbon atoms:

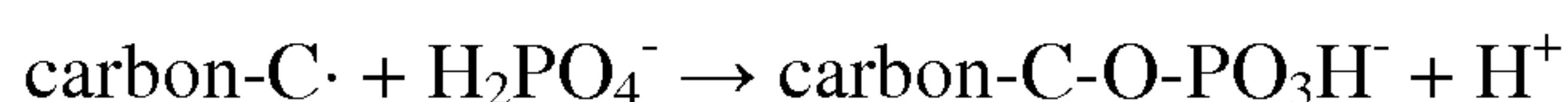
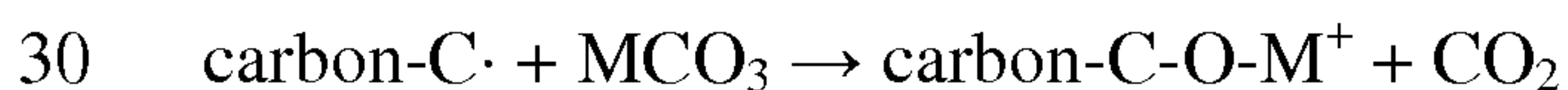


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Subsequently these hydroxyl groups can react with transition metal M = Mn or M or phosphate ions:



The coordinatively unsaturated carbon atoms created by milling can also react directly with the metal salt or phosphate ions:



Through these chemical reactions of the $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ precursors with the carbon surface nucleation centers are created for the growth of covalently bound, amorphous $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ by further mechanochemical reaction. On a carbon of very high specific surface area (as obtained by milling with high surface area carbon black or graphite) the amorphous $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ is very finely dispersed resulting in a nanocomposite of very small particle size after crystallization treatment and large-area electric contact with conductive carbon, which is crucial for good rate performance. Covalent binding of $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ to carbon through oxygen bridges (C-O-M or C-O-P) also improves the electric contact of the cathode active material with the current collector of the battery, which again is important to achieve high current densities. A stoichiometric excess of transition metal precursor during milling favors formation of a metal oxide bonding layer (C-O-M) between carbon and LiMPO_4 , while an excess of phosphate favors bonding by phosphate groups (C-O-P).

The presence of covalent bonds between $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ and carbon can be shown by different analytical techniques, such as infrared (FTIR) and Raman spectroscopy, or X-ray spectroscopy (e.g. XAFS, XANES, XPS). For example the formation of an intermediate manganese oxide bonding layer by ball-milling of nanocrystalline LiMnPO_4 with Ketjenblack® in presence of a small amount of water has been revealed by Raman spectroscopy.²⁷

Due to the intimate mixing of the $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ precursors by milling on the nanometer scale crystallization occurs already at moderate temperature (around 400°C). The low thermal diffusivity at such a low crystallization temperature results in the formation of very small nanocrystals. In addition, crystal growth is inhibited by the covalently bound carbon in the nanocomposite, which reduces the diffusivity even more. Hence a $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ /carbon nanocomposite with nanocrystalline $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ of less than about 100 nm crystallite size and intimate contact between nanocrystalline active material and conductive carbon is formed, which is a premise for excellent electrochemical performance.

The primary particle size of $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ in the nanocomposite can be determined by electron microscopy (SEM or TEM). The crystallite size of $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ can be calculated from the X-ray diffraction line broadening with the Scherrer equation, or more accurately with the Warren-Averbach method or by Rietveld refinement, in order to take into account the contribution of lattice strain to line broadening.

The relative mass of carbon required to obtain an average carbon coating thickness t on
 5 spherical lithium metal phosphate particles of average radius r is given by:

$$M_{\text{carbon}}/M_{\text{LiMPO}_4} = \rho_{\text{carbon}}/\rho_{\text{LiMPO}_4} \cdot [(1+t/r)^3 - 1]$$

For $r = 20$ nm and $t = 1$ nm with $\rho_{\text{carbon}} = 2.2$ g/cm³ and $\rho_{\text{LiMPO}_4} = 3.5$ g/cm³:
 10

$$M_{\text{carbon}}/M_{\text{LiMPO}_4} = 0.1$$

Hence for spherical $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ particles of 40 nm average diameter and a continuous
 dense carbon coating of 1 nm mean thickness 10 wt% carbon with respect to the mass of
 15 $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ would be required. The necessary amount would be higher for non-
 spherical particles since a sphere has the smallest surface area for a given volume. It would be
 lower for bigger $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ particles or a thinner or discontinuous or less dense carbon
 coating.

20 Carbon exhibits higher electric conductivity when being in its graphite modification (sp^2
 hybridized carbon) and within the two-dimensional basal graphene planes. Hence for good
 electric conductivity of the carbon network in the nanocomposite a large fraction and
 sufficient extension of these graphitic domains with sp^2 carbon is preferred. Since the low
 heat treatment temperature of 350-600°C is not sufficient to cause any graphitization a high
 25 graphene fraction is advantageously already present in the carbon additive before milling.
 According to the present invention this is achieved by employing electro-conductive carbon
 black of high surface area, such as Printex® XE 2 (Evonik Degussa), Black Pearls® 2000
 (Cabot) or Ketjenblack® (Akzo Nobel), graphite with specific surface area of at least 9.5
 m²/g, expanded graphite, graphene, or activated carbon. The fraction and size of well
 30 conducting graphene domains in the nanocomposite obtained by milling can be determined by
 different analytical techniques, such as Raman spectroscopy (ratio of graphene G-band
 around 1580 cm⁻¹ and disorder D-band around 1360 cm⁻¹)^{67, 68}, X-ray and neutron diffraction,
 as well as electron microscopy (TEM).

The invention provides an electroactive lithium manganese phosphate material (LiMnPO_4) or solid solution $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ (where M is at least one other metal (e.g. Fe, Ni, Co, Cr, V, Mg, Ca, Al, B, Zn, Cu, Nb, Ti, Zr, La, Ce, Y) and $x = 0.8-1.1$ and $y = 0.5-1.0$ and $z = 0.9 < z < 1.1$) characterized in that it comprises a Metal oxide layer on the LiMnPO_4 material, respectively the $\text{LiMn}_y\text{M}_{x1-y}\text{PO}_4$ material. The oxide described above is between the LiMnPO_4 material, respectively the $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ material, and a conductive additive such as carbon. The presence of the oxide layer is demonstrated by Raman spectroscopy.

In contrast to other methods to prepare manganese oxide interface layer between the $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ material, and the carbon layer, this novel method prepares both the $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ material and the interface layer in-situ from precursors of $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$.

It has been demonstrated that the the presence of a manganese oxide interface layer between the LiMnPO_4 material, and the carbon layer improved electrochemical performance.

The manganese oxide layer is shown to be either Mn_3O_4 (hausmanite), $\beta\text{-MnO}_2$ (pyrolusite), MnO (manganosite), MnOOH (groutite) or $\text{Mn}_{1.85}\text{O}_{0.6}\text{H}_2\text{O}$ (birnessite). The method to prepare the manganese oxide interface layer required a ready-made LiMnPO_4 and milled it with a carbon source. In no cases were pre-cursors of LiMnPO_4 and carbon milled to form in-situ both the LiMnPO_4 and the manganese oxide interface layer between the LiMnPO_4 material, and the carbon layer.

According to the state of the art lithium metal phosphates LiMPO_4 should contain metals M and phosphate PO_4 in stoichiometric ratio $\text{M}/\text{PO}_4 = 1$ in order to form a pure single phase material. Any deviations from nominal stoichiometry generally result in the formation of impurity phases that diminish electrochemical performance.

Surprisingly we found that significant stoichiometric excess 1-10% of phosphate can be accommodated in the case of nanocrystalline LiMPO_4 without loss in performance. This is achieved, by for example adding a stoichiometric excess of LiH_2PO_4 as a reactant. Due to the very high specific surface area of nanocrystalline LiMPO_4 excess phosphate is incorporated into the crystal surface and forms a phosphate terminated surface. Such a phosphate termination can offer several advantages (Figures 15 to 17):

1. Phosphate termination favours formation of strong bonds between carbon coating and lithium metal phosphate: this results in better adhesion and electric contact.
2. Phosphate termination protects the metal ions Mn and M from oxidation during handling of the material in air.
- 5 3. Phosphate termination prevents exposure of the metal ions Mn and M to the electrolyte and thus their dissolution and subsequent reduction at the anode, which results in enhanced stability at elevated temperature.
4. Phosphate termination reduces catalytic oxidation of the electrolyte by avoiding direct contact with the transition metal ions Mn and M, which improves stability at high voltage and
- 10 temperature.

Calculation of phosphate excess:

The molar phosphate excess required for complete phosphate termination of a spherical
15 lithium metal phosphate particle of radius r can be calculated from basic geometry as

$$\frac{n_{surface}}{n_{volume}} = \frac{3}{r} \cdot \sqrt[3]{\frac{M}{\rho \cdot N_A}}$$

with

20 $n_{surface}$ = average number of lithium metal phosphate formula units in the particle surface

n_{volume} = number of lithium metal phosphate formula units in the particle volume

r = particle radius

M = molar mass of lithium metal phosphate

ρ = density of particle

25 N_A = Avogadro's number

For example in the case of a spherical $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ nanoparticle of 50 nm diameter:

$r = 25 \text{ nm}$, $M = 158 \text{ g/mol}$, $\rho = 3.4 \text{ g/cm}^3$ gives $n_{surface} / n_{volume} = 0.05$

Hence a phosphate excess of 5 mol% would be necessary for complete phosphate termination
30 of this nanoparticle.

Since the real lithium metal phosphate powder consists of non-spherical particles with a distribution of sizes this is only an approximation. The optimum phosphate excess has to be determined experimentally. Too low phosphate excess results in partial phosphate termination where part of the transition metal ions remain exposed at the surface (Figure 15b). This will not offer the full advantages of a complete phosphate termination (Figure 15c). On the other hand too large phosphate excess will form a thicker layer with diphosphate (Figure 15d) or higher phosphate oligomers on the particle surface. This impedes both electron exchange with the carbon coating and lithium exchange with the electrolyte and thereby degrades battery performance at high charge or discharge rate.

Figure 18 shows the electrochemical performance of a lithium battery with $\text{Li}_{1.04}\text{Mn}_{0.8}\text{Fe}_{0.2}(\text{PO}_4)_{1.04}/10\%\text{C}$ nanocomposite containing 4% excess lithium phosphate (Example 7).

Increasing the phosphate excess in the material to 10% results in the appearance of new crystalline phases, such as $\text{Li}_2\text{P}_2\text{O}_7$ and other polyphosphates, which can be detected by X-ray diffraction (Fig. 19). These new crystalline phases may have benefits including improved electrochemical stability, but may have a reduced electrochemical capacity.

EXAMPLES

5 **Example 1:** Synthesis of LiMnPO_4/C nanocomposite

A mixture of 3.45 g MnCO_3 (Aldrich 99.9%) + 3.12 g LiH_2PO_4 (Aldrich 99%) + 1 g Ketjenblack® EC600JD (Akzo Nobel) was milled in a hardened steel container of 250 mL capacity with 12 hardened steel balls of 20 mm diameter in a planetary ball mill (Retsch PM
10 100) at 500 rpm for 2 hours. The obtained powder was heated up to 450°C within 30 minutes and maintained at this temperature for 1 hour under a stream of argon + 8% hydrogen.

Example 2: Synthesis of $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$ nanocomposite (18% Ketjenblack®)

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A mixture of 3.105 g MnCO_3 (Aldrich 99.9%) + 0.54 g $\text{FeC}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ (Fluka 99%) + 3.12 g LiH_2PO_4 (Aldrich 99%) + 1 g Ketjenblack® EC600JD was milled as described in Example 1 and heated at 350, 450 or 550°C for 1 hour under argon + 8% hydrogen.

Figure 1 shows a scanning electron microscope picture of the nanocomposite obtained at
20 450°C , indicating a primary particle size in the order of 50 nm for the brighter $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ component.

Figure 2 shows the X-ray diffraction patterns of the three samples, indicating poor crystallization after 1 hour at 350°C , while the sample heated for the same time at 450°C is well crystallized $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ without any apparent impurities. From the line broadening
25 an average crystallite size of 60 nm with negligible strain was calculated with the Warren-Averbach method. This agrees with the primary particle size in the order of 50 nm observed in the SEM picture (Figure 1).

30

Table 1

Lattice parameters	LiMn _{0.8} Fe _{0.2} PO ₄ / 10% Ketjenblack EC600JD	LiMn _{0.8} Fe _{0.2} PO ₄ (Yamada 2001)	Reference LiMnPO ₄	Reference LiFePO ₄
a	10.419 Å	10.44 Å	10.446 Å	10.34 Å
b	6.079 Å	6.09 Å	6.103 Å	6.01 Å
c	4.731 Å	4.736 Å	4.744 Å	4.692 Å
V	299.70 Å ³	301.6 Å ³	302.44 Å ³	291.6 Å ³

5 **Example 3:** Synthesis of LiMn_{0.8}Fe_{0.2}PO₄/10%C nanocomposites with different carbon materials

A mixture of 2.76 g MnCO₃ (Aldrich 99.9%) + 1.08 g FeC₂O₄·2 H₂O (Fluka 99%) + 3.12 g LiH₂PO₄ (Aldrich 99%) + 0.5 g carbon was milled and heat treated as described in Example 1.

Following carbon materials were compared:

Ketjenblack® EC-300J (Akzo Nobel, 800 m²/g)

Ketjenblack® EC-600JD (Akzo Nobel, 1400 m²/g)

Printex®. XE 2 (Degussa, 950 m²/g)

15 Black Pearls ® 2000(Cabot, 1500 m²/g)

Shawinigan acetylene black C-55 (70 m²/g)

Vulcan XC 72R (270 m²/g)

Multi walled carbon nanotubes (MWCNT)

High surface graphite Timrex® HSAG300 (Timcal, 280 m²/g)

20 Timrex® KS4 graphite (Timcal, 26 m²/g)

Timrex® KS6 graphite (Timcal, 20 m²/g)

Timrex® SFG6 graphite (Timcal, 17 m²/g)

Timrex® MB15 graphite (Timcal, 9.5 m²/g)

Norit® DLC Super 50 activated carbon (Norit, 1600 m²/g)

Example 4: Synthesis of $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/10\%\text{C}$ nanocomposites with a combination of carbon materials

A mixture of 5.52 g MnCO_3 (Aldrich 99.9%) + 2.16 g $\text{FeC}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ (Fluka 99%) + 6.24 g
 5 LiH_2PO_4 (Aldrich 99%) + 0.8 g Cellulose (Aldrich, microcrystalline) + 0.4 g Ketjenblack®
 EC600JD (Akzo Nobel) + 0.4 g Timrex® SFG 44 graphite (Timcal) was milled in a
 hardened steel container of 250 mL capacity with 12 hardened steel balls of 20 mm diameter
 in a planetary ball mill (Retsch PM 100) at 500 rpm for 2 hours. The obtained powder was
 heated up to 600°C within 10 minutes and maintained at this temperature for 20 minutes
 10 under a stream of argon.

Example 5: Synthesis of $\text{LiMn}_{0.9}\text{V}_{0.05}(\text{PO}_4)_{0.9}(\text{VO}_4)_{0.05}/10\%\text{C}$ nanocomposite

A mixture of 6.21 g MnCO_3 (Aldrich 99.9%) + 0.636 g LiVO_3 (Alfa Aesar 99.9%) + 5.62 g
 15 LiH_2PO_4 (Aldrich 99%) + 1 g Ketjenblack® EC600JD was milled in a hardened steel
 container of 250 mL capacity with 12 hardened steel balls of 20 mm diameter in a planetary
 ball mill (Retsch PM 100) at 400 rpm for 2 hours. The obtained powder was heated up to
 500°C within 10 minutes and maintained at this temperature for 20 minutes under a stream of
 argon.

20

Example 6: Synthesis of $\text{LiMn}_{0.9}\text{Ti}_{0.1}\text{PO}_4/10\%\text{C}$ nanocomposite

A mixture of 6.21 g MnCO_3 (Aldrich 99.9%) + 1.77 g $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ (Aldrich
 99.998%) + 6.24 g LiH_2PO_4 (Aldrich 99%) + 1 g Ketjenblack® EC600JD was milled in a
 25 hardened steel container of 250 mL capacity with 12 hardened steel balls of 20 mm diameter
 in a planetary ball mill (Retsch PM 100) at 400 rpm for 2 hours. The obtained powder was
 heated up to 500°C within 10 minutes and maintained at this temperature for 20 minutes
 under a stream of argon.

30

Example 7: Synthesis of $\text{Li}_{1.04}\text{Mn}_{0.8}\text{Fe}_{0.2}(\text{PO}_4)_{1.04}/10\%\text{C}$ nanocomposites with 4% excess lithium phosphate

A mixture of 2.62 g MnCO_3 (Aldrich 99.9%) + 1.08 g $\text{FeC}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ (Fluka 99%) + 3.12 g LiH_2PO_4 (Aldrich 99%) + 0.5 g Timrex SFG 6L graphite (Timcal) was milled and heat treated as described in Example 1.

5 **Figure 21.** trace c and d show the Raman spectra of samples prepared with 5 and 10% excess of LiH_2PO_4 described in Experiment 7 respectively. They are compared to an equivalent material prepared with no phosphate excess (curve b) as per in example 3). Excitation wavelength 633 nm The change in spectra versus curve b example 3 is illustrative of a different interface.

10

Example 8: Preparation of $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z/\text{C}$ cathodes and secondary lithium batteries with such cathodes

1 g of $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ nanocomposite as obtained in the above Examples was mixed with
 15 20 mg carbon nano fibers (CNF) and 75 mg PVdF (polyvinylidene difluoride) in NMP (N-methyl-2-pyrrolidinon). This dispersion was doctor bladed on a carbon coated aluminum foil and dried at 120°C under vacuum. The electrodes were compressed into $\varnothing$ 23 mm disks with a thickness of about 30 μm and an active material loading of about $3.0 \text{ mg}/\text{cm}^2$. Cells were assembled in SwagelokTM fittings using Li metal foil as counter electrode with a microporous
 20 polymer separator (Celgard 2400TM) and an electrolyte of 1M LiPF_6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) 1:1 (by volume) + 1% VC.

The electrochemical properties of the $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ electrodes were measured by galvanostatic charge/discharge and cyclic voltammetry with Arbin BT 2000. Figures 3, 5, 7 and 8 show the electrochemical performance at different discharging rates. Figures 4 and 6
 25 show the stability on cycling at a charge/discharge rate of 1 C.

Example 9:

Pure LMP/carbon was prepared by solid state reaction.

A mixture of 3.45 g MnCO_3 (Aldrich 99.9%) + 3.12 g LiH_2PO_4 (Aldrich 99%) + 1 g
 30 Ketjenblack® EC600JD (Akzo Nobel) was milled in a hardened steel container of 250 mL capacity with 12 hardened steel balls of 20 mm diameter in a planetary ball mill (Retsch PM 100) at 500 rpm for 2 hours. The obtained powder was heated up to 450°C within 30 minutes and maintained at this temperature for 1 hour under a stream of argon + 8% hydrogen. Alternatively 20% of MnCO_3 was exchanged with Mn-oxalate.

Figure 20 shows the spectra (Labram HR, Horiba Jobin-Yvon, $\lambda=633$ nm) of pure LMP/carbon prepared by solid state reaction as described in example 9, in one case with 20% of Mn-oxalate (curve e and f), in the other case without Mn-oxalate (curve c and d). In each case, two laser powers are used (D0.6 means higher laser power). For comparison, spectra of hausmannite Mn_3O_4 (b) and also MnO_2 (a).

In all LMP spectra, the band at ca 645 cm^{-1} is present. It has the highest relative intensity in LMP without Mn-oxalate taken at lower laser power. The same sample measured at a higher laser power shows relatively weak signal of Mn_3O_4 . The sample prepared with 20% of Mn-oxalate shows very similar spectra under both laser powers. The parameters of the possible Mn-O bands in the sample without Mn-oxalate at lower laser power (spectrum d in Fig. 20) are very close to those of hausmannite in terms of position and FWHM. In the other LMP spectra, these bands are more downshifted and broadened, towards “ MnO_2 ” spectrum.

The close resemblance of its peak pattern to hausmannite is evident, albeit not unambiguous. Lower symmetry and/or presence only in a thin layer on the LMP-carbon interface can be also responsible for some peak broadening and downshifting compared to hausmannite. The sharpness of the Mn-O bands in LMP without Mn-oxalate even at lower laser power indicates that this manganese oxide has not been generated by the laser-induced heating.

A partial presence of another Mn-oxide, e.g. bixbyite, $(\text{Mn,Fe})_2\text{O}_3$, cannot be ruled out. The loss of Mn-O signal with increasing laser power in this sample (without Mn-oxalate) is intriguing, as well as almost the same signal in the other sample (with Mn-oxalate) at both laser powers.

Example 10

A mixture of 2.76 g MnCO_3 (Aldrich 99.9%) + 1.08 g $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Fluka 99%) + 3.12 g LiH_2PO_4 (Aldrich 99%) + 0.5 g Ketjenblack® EC600JD was milled as described in Example 1 and heated at 450°C for 1 hour under argon/ H_2 atmosphere. A comparative experiment was prepared with the same conditions, except that the same amount of Vulcan XC72R or Shawinigan acetylene black C-55 was used in place of Ketjenblack® EC600JD (Akzo Nobel)

The characterization data and the electrochemical performance are given in Table2. The electrochemical performance of cathode material prepared with Ketjenblack® EC600JD (Akzo Nobel) is close to theoretical value, whereas the cathode material prepared with

Shawinigan acetylene black C-55 show lower electrochemical performance and the material prepared with Vulcan XC72-R is electrochemical inactive.

In Fig. 22 show Raman spectra of these three cathode materials. The $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ cathode material prepared with Ketjenblack® EC600JD (Akzo Nobel) show the most intensive hausmannite signal at about 650nm, while the material $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ prepared with Vulcan XC72R does not contain this signal.

10

Table 2: Characterization and electrochemical performance of $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ cathode material prepared with Ketjenblack 600 , Acetylene black C55 and Vulcan 72R respectively

Sample	$\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ + 10% carbon:	Carbon BET m ² /g	Sample BET m ² /g	a/Å	b/Å	c/Å	V/Å ³	Cryst. size nm	Capacity @ 1 C (mAh/g)
v150208	Ketjenblack EC- 600JD	1400	88	10.420	6.081	4.736	300.2	51	132
f26020	acetylene black C- 55	70	35	10.416	6.073	4.733	299.4	52	99
g150208	Vulcan XC 72R	270	46	10.424	6.081	4.736	300.2	47	0

15

The figures are discussed in more detailed manner below :

Figure 1a shows a high resolution scanning electron microscope (HRSEM) picture of the $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$ nanocomposite (18% Ketjenblack EC600JD) according to Example 2 after heating for 1 hour under argon/8% hydrogen at 450°C. The primary particle size is in the order of 50 nm for the brighter $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ component.

Figure 1b shows a HRSEM picture of the $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ nanocomposite (10% Ketjenblack EC600JD) according to Example 3.

25

Figure 1c shows a TEM picture of the $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ nanocomposite (10% Ketjenblack EC600JD) according to Example 3.

Figure 2a shows the X-ray diffraction (XRD) patterns of the $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$ nanocomposite (18% Ketjenblack EC600JD) according to Example 2 after heating for 1 hour under argon/8% hydrogen at different temperatures. Only weak XRD peaks are observed after 1 hour at 350°C indicating poor crystallization, while the sample heated for the same time at 450°C is well crystallized $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ without any apparent impurities. Heating at 550°C leads to a further increase in the peak intensities and slight reduction in the peak widths. From the line broadening at 450°C an average crystallite size of 60 nm with negligible strain was calculated with the Warren-Averbach method. This agrees with the primary particle size in the order of 50 nm observed in the SEM picture (Figure 1).

Figure 2b shows the XRD pattern of the $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ nanocomposite (10% Ketjenblack EC600JD)) with Rietveld refinement according to Example 3 and Table 1 the crystal data from the XRD pattern.

Mean crystallite size from XRD line broadening $L = 51 \text{ nm}$

BET surface area $A = 88 \text{ m}^2/\text{g}$

Figure 3 represents the electrochemical performance of two different lithium batteries with $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$ nanocomposite cathode (18% Ketjenblack EC600JD, Example 2) at different discharge rates on cycling between 2.7 and 4.4 V against lithium. A capacity of 150 mAh/g of active material is achieved at D/10. Even at a discharge rate of 5D a capacity as high as 130 mAh/g is obtained.

Figure 4 shows the cycling stability (at 1 C and C/10 each 10th cycle, charged up to 4.25 V) of the lithium batteries from Figure 3 with $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$ nanocomposite cathode (18% Ketjenblack EC600JD, Example 2).

Figure 5 shows the electrochemical performance of a lithium battery with $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ nanocomposite cathode (10% Ketjenblack EC600JD, Example 3) at different discharge rates on cycling between 2.7 and 4.4 V against lithium. A capacity of 145 mAh/g of active material is obtained at D/10. At a discharge rate of 5D the capacity is still higher than 110 mAh/g.

Figure 6a shows the cycling stability at 21°C (discharge rate 1 C and C/10 each 10th cycle, charged up to 4.25 V) of a lithium battery according to Figure 5 with $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ nanocomposite cathode (10% Ketjenblack EC600JD, Example 3).

Charging condition: CCCV 2.7 - 4.25V vs. Li

- 5 Discharge: C rate calculated from 150mAh/g
- Cathode: $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C} + 2\% \text{ CNF} + 7.5\% \text{ PVDF}$
- Loading: 2.7 mg/cm^2
- Electrolyte: LP30 + 1% VC

10 **Figure 6b** shows the cycling stability at 50°C (discharge rate 5 C, charged up to 4.25 V) of a lithium battery according to Figure 5 with $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ nanocomposite cathode (10% Ketjenblack EC600JD, Example 3).

Charging condition: CCCV 2.7 - 4.25V vs. Li

- Discharge: C rate calculated from 150mAh/g
- 15 Cathode: $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C} + 2\% \text{ CNF} + 7.5\% \text{ PVDF}$
- Loading: 5.4 mg/cm^2
- Electrolyte: LP30 + 1% VC

Figure 7 shows the electrochemical performance of lithium batteries with $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/10\%\text{C}$ nanocomposite cathodes prepared from different carbon sources (Example 3) on cycling between 2.7 and 4.4 V against lithium:

- △ Ketjenblack EC-300J (Akzo Nobel, $800 \text{ m}^2/\text{g}$)
 - Ketjenblack EC-600JD (Akzo Nobel, $1400 \text{ m}^2/\text{g}$)
 - ▲ Black Pearls 2000 (Cabot, $1500 \text{ m}^2/\text{g}$)
 - 25 ◆ Multi walled carbon nanotubes (MWCNT)
 - High surface graphite Timrex HSAG300 (Timcal, $280 \text{ m}^2/\text{g}$)
- Ketjenblack EC-600JD and high surface graphite Timrex HSAG300 show the best performance with a capacity of 145 mAh/g at D/10 and more than 110 mAh/g at 5D.

30 **Figure 8** shows the electrochemical performance of lithium batteries with $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/10\%\text{C}$ nanocomposite cathodes prepared from different carbon sources (Example 3) on cycling between 2.7 and 4.4 V against lithium:

- ▲ Ketjenblack EC-600JD (Akzo Nobel, $1400 \text{ m}^2/\text{g}$)
- ◆ Timrex KS4 graphite (Timcal, $26 \text{ m}^2/\text{g}$)

◇ Timrex SFG6 graphite (Timcal, 17 m²/g)

□ Timrex MB15 graphite (Timcal, 9.5 m²/g)

Δ Shawinigan acetylene black C-55 (70 m²/g)

The three different graphites yield comparable performance to Ketjenblack EC-600JD.

5 Shawinigan acetylene black C-55 gives much lower capacity, especially at higher discharge rates.

Figure 9

10 Raman spectra of pure carbons and LiMn_{0.8}Fe_{0.2}PO₄/ 10% carbon nanocomposites (Example 3) in the region of the graphitic G band around 1600 cm⁻¹ and the disordered carbon D band around 1350 cm⁻¹.

The carbons are:

KB600: Ketjenblack EC600JD (Akzo Nobel, 1400m²/g)

KB300: Ketjenblack EC300J (Akzo Nobel, 800m²/g)

15 C55: Shawinigan acetylene black (70m²/g)

KS6: Timrex graphite (Timcal, 20m²/g)

Figure 10

20 Cyclic voltammogram of LiMn_{0.8}Fe_{0.2}PO₄/C nanocomposite cathode (10% Ketjenblack EC600JD, Example 3)

Figure 11

Discharge curves of a lithium battery with LiMn_{0.8}Fe_{0.2}PO₄/C nanocomposite cathode (10% Ketjenblack EC600JD, Example 3) at 21°C

25 Charging condition: CCCV 2.7 - 4.4 V vs. Li

Discharge: C rate calculated from 150mAh/g

Electrode: LiMn_{0.8}Fe_{0.2}PO₄/C + 2% CNF + 7.5% PVDF

Loading: 4.6 mg/cm²

Electrolyte: 1M LiPF₆ / EC / DMC 1:1 + 2% VC

30

Figure 12

Discharge curves of a lithium battery with LiMn_{0.8}Fe_{0.2}PO₄/C nanocomposite cathode (10% Ketjenblack EC600JD, Example 3) at 50°C

Charging condition: CCCV 2.7 - 4.4 V vs. Li

Discharge: C rate calculated from 150mAh/g
 Electrode: $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C} + 2\% \text{ CNF} + 7.5\% \text{ PVDF}$
 Loading: 4.4 mg/cm^2
 Electrolyte: $1\text{M LiPF}_6 / \text{EC} / \text{DMC } 1:1 + 1\% \text{ VC}$

5

Figure 13

Cell charge status for XRD analysis

Electrode from coin cell

0.1C for 2~3 cycles

10 2.0V: 0.01C discharge and CV to 2.0V $\rightarrow \text{Li}_{\approx 1}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$

3.4V: 0.1C charge and CV to 3.4V $\rightarrow \text{Li}_{\approx 0.95}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$

4.0V: 0.1C charge and CV to 4.0V $\rightarrow \text{Li}_{\approx 0.7}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$

4.4V: 0.1C charge and CV to 4.4V $\rightarrow \text{Li}_{\approx 0}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$

After CV, dismount the coin cell and clean with EMC then dry in vacuum oven with 60°C

15

Figure 14

XRD patterns of the cathode at different states of charge

2.0V $\rightarrow \text{Li}_{\approx 1}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$

3.4V $\rightarrow \text{Li}_{\approx 0.95}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$

20 4.0V $\rightarrow \text{Li}_{\approx 0.7}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$, still single olivine phase with reduced lattice parameters

4.4V $\rightarrow \text{Li}_{\approx 0}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$, new phase

Figure 15

Schematic side view of the lithium metal phosphate particle surface with different

25 terminations (the charge compensating lithium ions are omitted for clarity)

Figure 16

Simplified two-dimensional representation of the lithium metal phosphate lattice with a) stoichiometric surface and b) the same surface with phosphate termination (in the real three-dimensional lattice the metal ions M have octahedral coordination).

30

Figure 17

Simplified two-dimensional representation of the lithium metal phosphate lattice with a) metal hydroxide terminated surface and b) the same surface with phosphate termination (in the real three-dimensional lattice the metal ions M have octahedral coordination).

5

Figure 18 shows the electrochemical performance of a lithium battery with $\text{Li}_{1.04}\text{Mn}_{0.8}\text{Fe}_{0.2}(\text{PO}_4)_{1.04}/10\%\text{C}$ nanocomposite containing 4% excess lithium phosphate (Example 7).

10 **Figure 19** shows the XRD patterns of $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ nanocomposites (10% Ketjenblack EC600JD) with stoichiometric composition and 5%, respectively 10% excess LiH_2PO_4

Figure 20 show the Raman spectra of pure LiMnPO_4 + carbon prepared as described in example 9, in one case with 20% of Mn-oxalate (curve e and f), in the other case without Mn-oxalate (curve c and d), together with MnO_2 (curve a) and hausmannite Mn_3O_4 from Aldrich (curve b). Spectrum (c) is LMP without Mn-oxalate, sample F101_B_5. Spectrum (d) is LMP without Mn-oxalate, sample F101_B_6. Spectrum (e) is LMP with Mn-oxalate, sample F101_A_4. Spectrum (f) is LMP with Mn-oxalate, sample F101_A_5. In each case, two laser powers are used (D0.6 means higher laser power). Excitation wavelength 633 nm. The spectra are offset for clarity. The spectra are normalized to the intensity of the $\square_1(\text{PO}_4)$ band (in the case of LMP samples).

Both the measured manganese oxides (curve a and b) are characterized by an intense band at around 640-650 cm^{-1} , and a few less intense bands between 300 and 500 cm^{-1} . In the case of MnO_2 , all the bands are very broad and downshifted. Moreover, some other bands are present, e.g. at 520 cm^{-1} . The explanation for the similarity is based upon the highest stability against the laser of hausmannite amongst manganese oxides. Therefore, some of other manganese oxides tend to verge into Mn_3O_4 during the Raman observation. In all LMP spectra, the band at ca 645 cm^{-1} is present. It has the highest relative intensity in LMP without Mn-oxalate taken at lower laser power. On the other hand, the same sample measured at a higher laser power shows relatively weak signal of Mn_3O_4 . The sample prepared with 20% of Mn-oxalate shows very similar spectra under both laser powers. The parameters of the possible Mn-O bands in the sample without Mn-oxalate at lower laser power (spectrum d in

Fig. 20) are very close to those of hausmannite in terms of position and FWHM. In the other LMP spectra, these bands are more downshifted and broadened, towards “MnO₂” spectrum.

The close resemblance of its peak pattern to hausmannite is evident, albeit not unambiguous.

Lower symmetry and/or presence only in a thin layer on the LMP-carbon interface can be also

5 responsible for some peak broadening and downshifting compared to hausmannite. The sharpness of the Mn-O bands in LMP without Mn-oxalate even at lower laser power indicates that this manganese oxide has not been generated by the laser-induced heating.

10 A partial presence of another Mn-oxide, e.g. bixbyite, (Mn,Fe)₂O₃, cannot be ruled out. The loss of Mn-O signal with increasing laser power in this sample (without Mn-oxalate) is intriguing, as well as almost the same signal in the other sample (with Mn-oxalate) at both laser powers.

15 **Figure 21** shows the spectra (Labram HR, Horiba Jobin-Yvon, λ 633 nm) of LMP/LFP/carbon mixtures prepared as described in Example 2 and Example 7, comparing two Calcination conditions which may lead to different amounts of oxidation interface.

Calcination in pure argon (curve A sample **HPLLMP66**) vs. argon/hydrogen (curve B, sample **HPLLMP67**). However, it was not possible to measure the two samples under the
20 same laser power. **HPLLMP66** (under Ar - Curve A) gave no signal besides carbon at D2, while **HPLLMP67** (under Ar/H₂- curve B showed optical changes (i.e. burning) during irradiation at D1. Though one accumulation spectrum at D1 was roughly similar to that at D2, a longer exposition to acquire a better quality spectrum was not possible. Such a varying reaction to the laser already points to a different nature of the Ar and Ar/H₂ calcined materials
25 and their interfaces.

The observed broadening of the bands in **HPLLMP66 curve A** is caused by the higher laser power. A slightly higher Fe₂O₃ signal in this sample and significantly more intense $\nu_4(\text{PO}_4)$ band at 625 cm⁻¹ in curve B, **HPLLMP67** (Ar/H₂) point to a more reduced state of sample calcined under Ar/H₂) and a more oxidized state of the sample calcined only under argon,
30 which was anticipated. This is indicative of a modified interface.

The curve c and d in Figure 21 show LMP/LFP/carbon mixtures prepared with 5 and 10% excess of LiH₂PO₄, respectively (same laser power) they are prepared as in Example 7. In this samples is the Fe₂O₃ and Mn₃O₄ signals less intensive but still obvious. The $\nu_1(\text{PO}_4)$

band is also narrower by 1.5 cm⁻¹ for 10% LiH₂PO₄ excess sample. The change in spectra versus curve b example 3 is illustrative of a different interface.

Fig. 22 shows Raman spectra of LiMn_yFe_{1-y}PO₄/C cathode material prepared in example 3 with Ketjenblack® EC600JD (Akzo Nobel) LiMn_yFe_{1-y}PO₄/C, Vulcan XC72R and Acetylene black C55 measured using LabRam HR, Horiba JY. The laser excitation wavelength was 633 nm and spectra are normalized to the ν_1 PO₄ vibration at 945 cm⁻¹.

Figure 23

10 HRTEM picture of LiMn_{0.8}Fe_{0.2}PO₄/C nanocomposite with 10% Ketjenblack® EC-600JD (Akzo Nobel, 1400 m²/g) (Example 3) showing intimate large-area contact between carbon and nanocrystalline active material (lattice fringes).

Figure 24

15 HRTEM picture of LiMn_{0.8}Fe_{0.2}PO₄/C nanocomposite with 10% Shawinigan acetylene black C-55 (70 m²/g) (Example 3) showing intact carbon black onions making only point contacts with prismatic nanocrystals of active material.

Figure 25

20 HRTEM picture of LiMn_{0.8}Fe_{0.2}PO₄/C nanocomposite with 10% Shawinigan acetylene black C-55 (70 m²/g) (Example 3) showing a carbon onion and a nanocrystal of active material (lattice fringes) without carbon coating.

Figure 26

25 HRTEM picture of LiMn_{0.8}Fe_{0.2}PO₄/C nanocomposite with 10% Vulcan XC 72R (270 m²/g) (Example 3) showing intact carbon onions.

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CLAIMS:

1. A lithium manganese phosphate/carbon nanocomposite suitable as a cathode material for rechargeable electrochemical cells, having the general formula $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z/\text{C}$ wherein:
 - 5 M is at least one other metal selected from the group consisting of Fe, Ni, Co, Cr, V, Mg, Ca, Al, B, Zn, Cu, Nb, Ti, Zr, La, Ce and Y;

$$x = 0.8-1.1;$$

$$y = 0.5-1.0; \text{ and}$$

$$0.9 < z < 1.1,$$
 - 10 with a carbon content of 0.5 to 20% by weight, obtained by heating and milling a precursor of $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ (lithium metal phosphate) with:
 - (a) electro-conductive carbon black having a specific surface area of at least $80 \text{ m}^2/\text{g}$;
 - (b) graphite having a specific surface area of at least $9.5 \text{ m}^2/\text{g}$; or
 - 15 (c) activated carbon having a specific surface area of at least $200 \text{ m}^2/\text{g}$.
2. The lithium manganese phosphate/carbon nanocomposite according to claim 1, wherein the lithium metal phosphate precursor is milled with the carbon black or the graphite and subsequently heated for crystallization.
3. The lithium manganese phosphate/carbon nanocomposite according to claim 1
 - 20 or 2, wherein the lithium metal phosphate precursor comprises a metal precursor, and a lithium precursor selected from the group consisting of LiH_2PO_4 , Li_2HPO_4 , LiPO_3 , Li_3PO_4 , Li_2O , LiOH , Li_2CO_3 and any other lithium compound that produces no byproducts which degrade the lithium manganese phosphate/carbon nanocomposite.

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4. The lithium manganese phosphate/carbon nanocomposite according to any one of claims 1-3, wherein the lithium metal phosphate precursor comprises a phosphate precursor selected from the group consisting of LiH_2PO_4 , Li_2HPO_4 , LiPO_3 , Li_3PO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$, phosphoric acid (HPO_3 or H_3PO_4) and any other phosphate compound that produces no
5 byproducts which degrade the lithium manganese phosphate/carbon nanocomposite.
5. The lithium manganese phosphate/carbon nanocomposite according to any one of claims 1-4, wherein the phosphate precursor is utilized in stoichiometric excess with respect to the lithium precursor and the metal precursor.
6. The lithium manganese phosphate/carbon nanocomposite according to any one
10 of claims 1-5, comprising oxygen bridges between the lithium metal phosphate and the carbon.
7. The lithium manganese phosphate/carbon nanocomposite according to claim 6, wherein the oxygen bridges consist of at least one metal oxide bonding layer.
8. The lithium manganese phosphate/carbon nanocomposite according to claim 7,
15 wherein the metal oxide bonding layer is a manganese oxide bonding layer.
9. The lithium manganese phosphate/carbon nanocomposite according to claim 8, wherein the manganese oxide bonding layer consists of Mn_3O_4 (hausmanite), 13-MnO_2 (pyrolusite), MnO (manganosite), MnOOH (groutite) or $\text{Mn}_{1.85}\text{O}_{6.6}\text{H}_2\text{O}$ (birnessite).
10. The lithium manganese phosphate/carbon nanocomposite according to claim 6,
20 wherein the oxygen bridges consist of at least one phosphate bonding layer.
11. The lithium manganese phosphate/carbon nanocomposite according to any one of claims 1-10, wherein the lithium precursor is added in stoichiometric excess in order to favor formation of the metal oxide bonding layer (C-O-M) between the carbon and the lithium metal phosphate.
- 25 12. The lithium manganese phosphate/carbon nanocomposite according to any one of claims 1-10, wherein the metal precursor is added in stoichiometric excess with respect to

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the phosphate precursor in order to favor formation of the metal oxide bonding layer (C-O-M) between the carbon and the lithium metal phosphate.

13. The lithium manganese phosphate/carbon nanocomposite according to any one of claims 1-10, wherein the phosphate precursor is added in stoichiometric excess with respect to the lithium precursor and the metal precursor in order to favor formation of the phosphate bonding layer between the carbon and the lithium metal phosphate.

14. The lithium manganese phosphate/carbon nanocomposite according to any one of claims 1-10, wherein the lithium precursor is added in stoichiometric excess with respect to the metal precursor in order to favor formation of the phosphate bonding layer between the carbon and the lithium metal phosphate.

15. The lithium metal phosphate/carbon nanocomposite according to any one of claims 1-14, wherein the $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ comprise particles having cross-sectional dimensions not larger than 200 nm as determined by electron microscopy.

16. The lithium metal phosphate/carbon nanocomposite according to any one of claims 1-15, wherein the average crystallite size of the $\text{Li}_x\text{Mn}_y\text{M}_{1-y}(\text{PO}_4)_z$ domains as determined by X-ray diffraction not larger than 100 nm.

17. A process for the production of a lithium manganese phosphate/carbon nanocomposite as defined in any one of claims 1-16, comprising heating and milling the lithium metal phosphate precursor with:

- (a) electro-conductive carbon black having a specific surface area of at least 80 m²/g;
- (b) graphite having a specific surface area of at least 9.5 m²/g; or
- (c) activated carbon having a specific surface area of at least 200 m²/g.

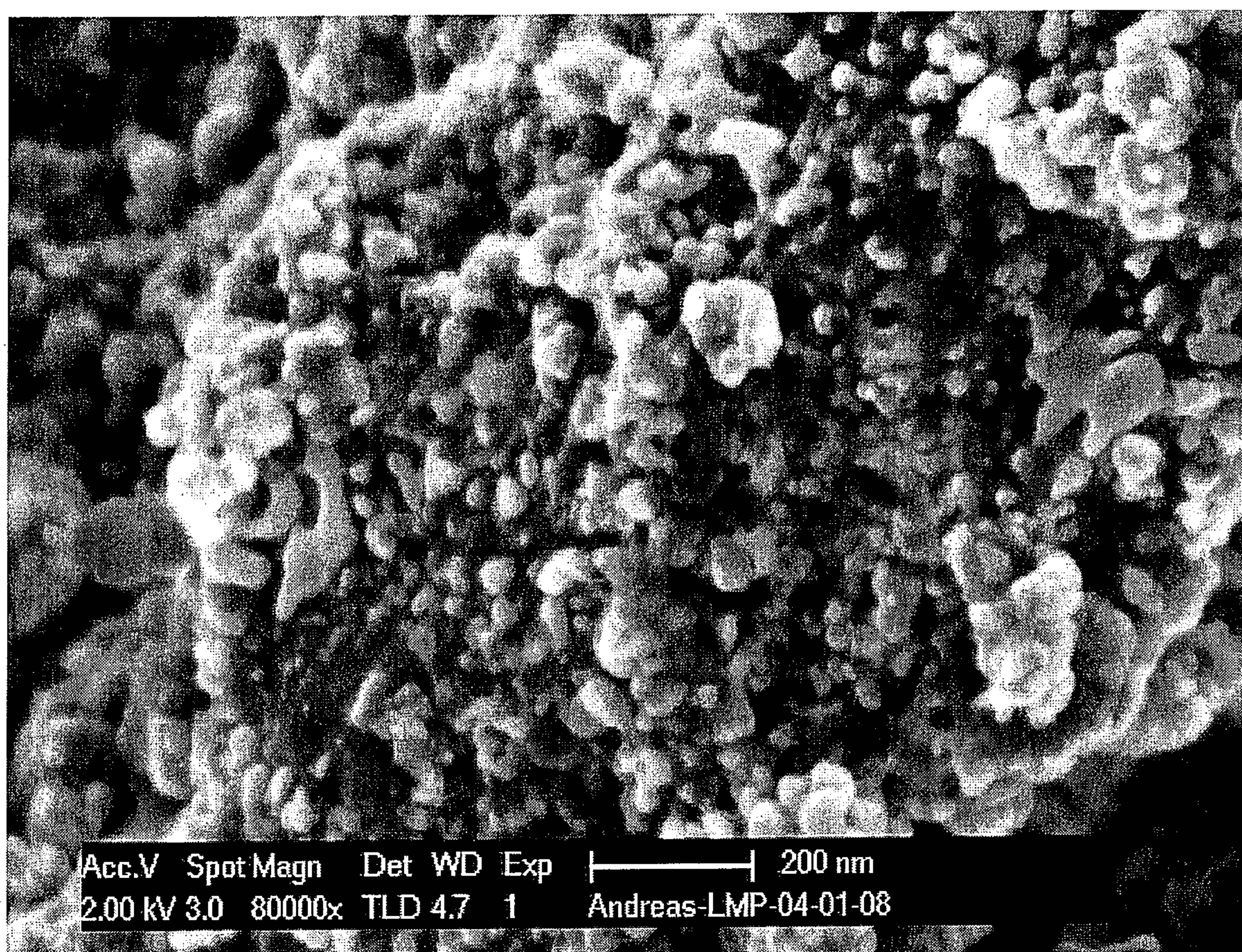


Figure 1a

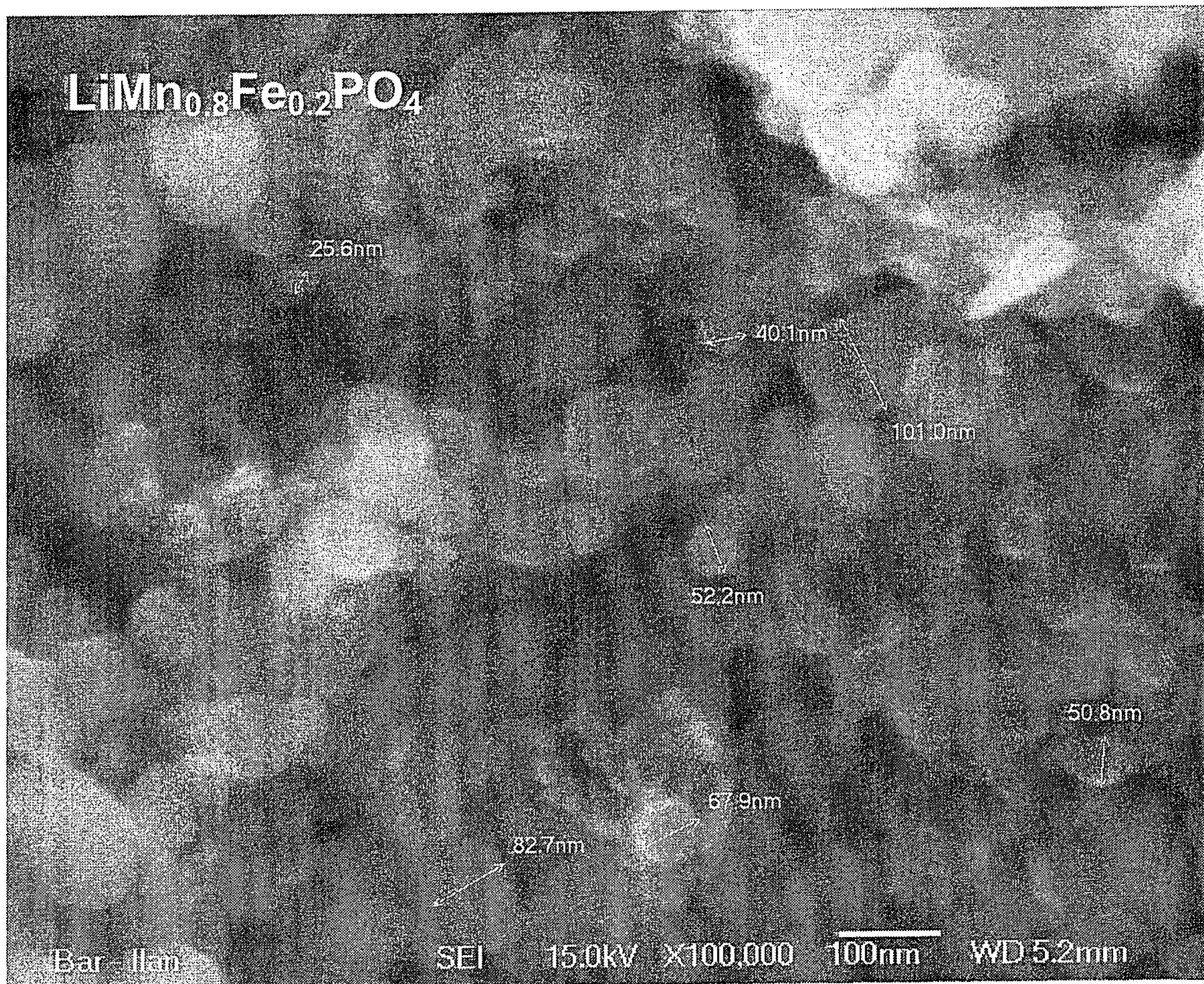
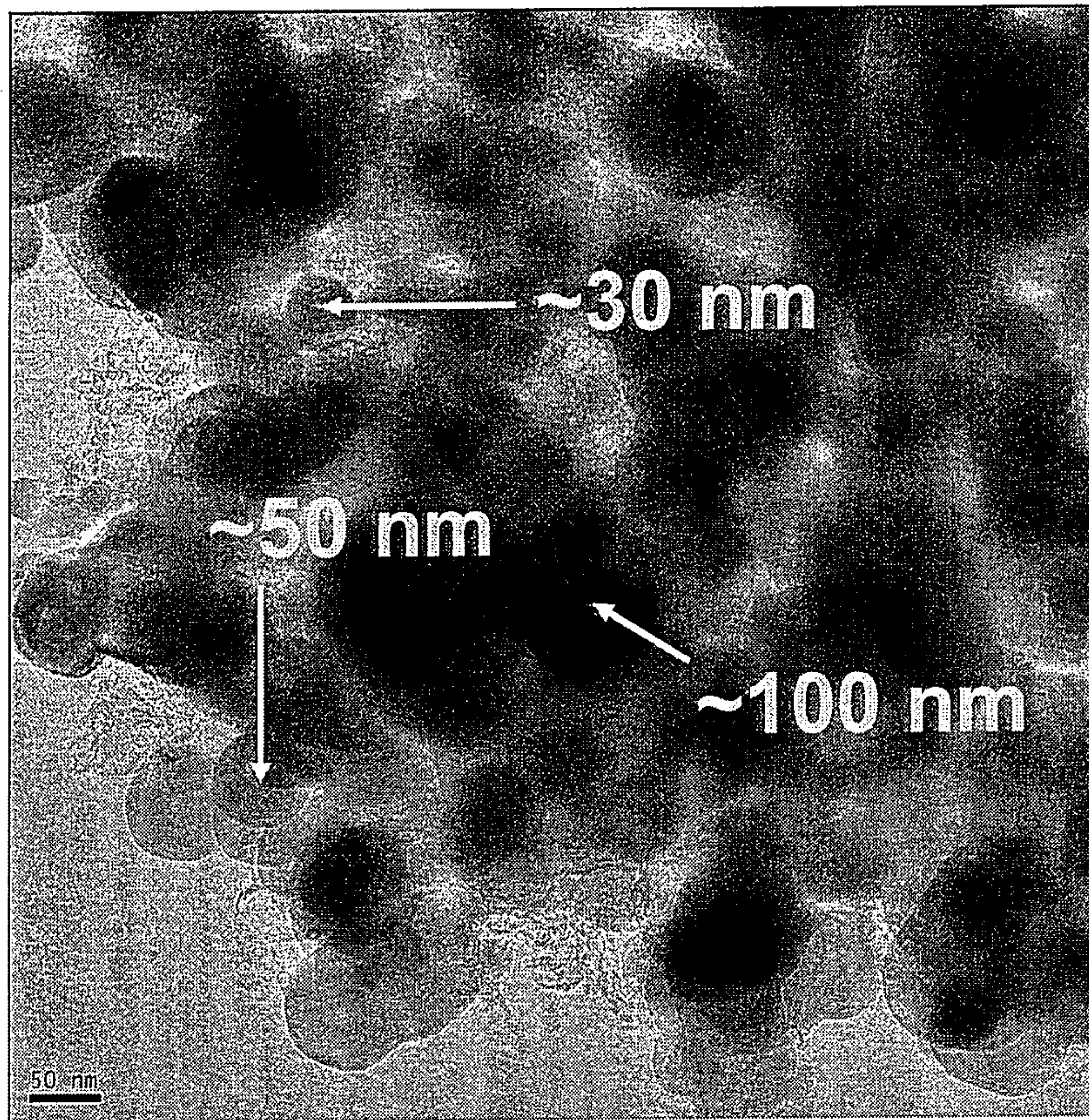


Figure 1b

**Figure 1c**

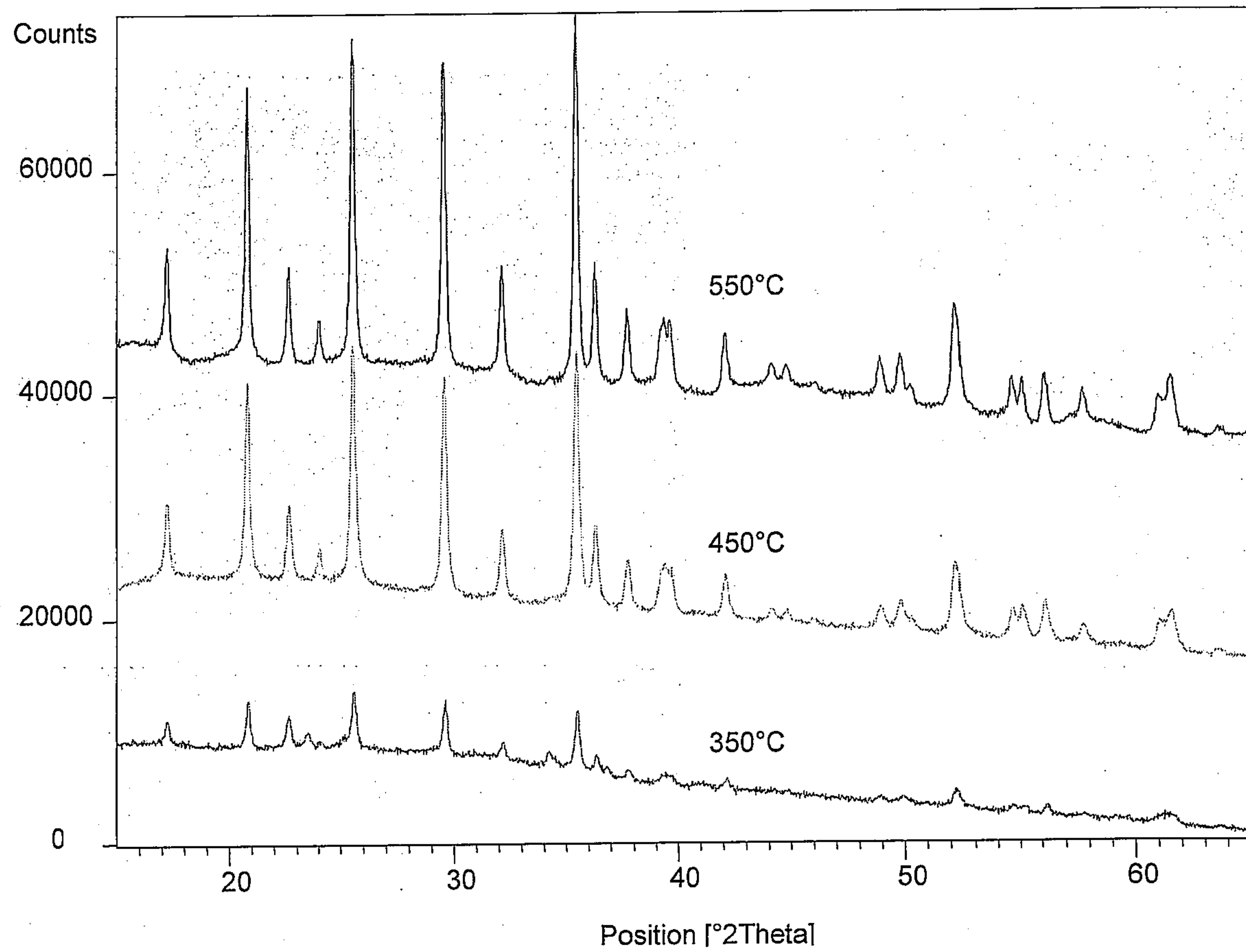


Figure 2a

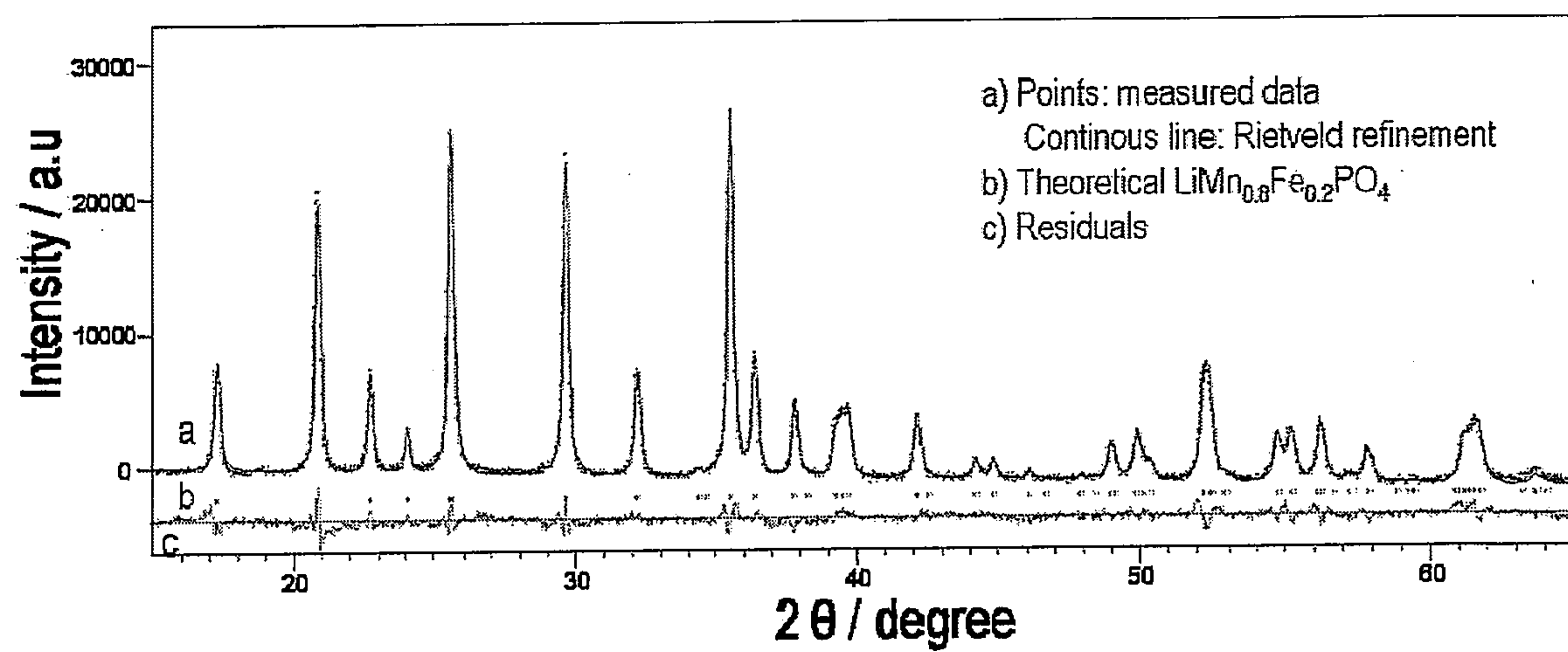


Figure 2b

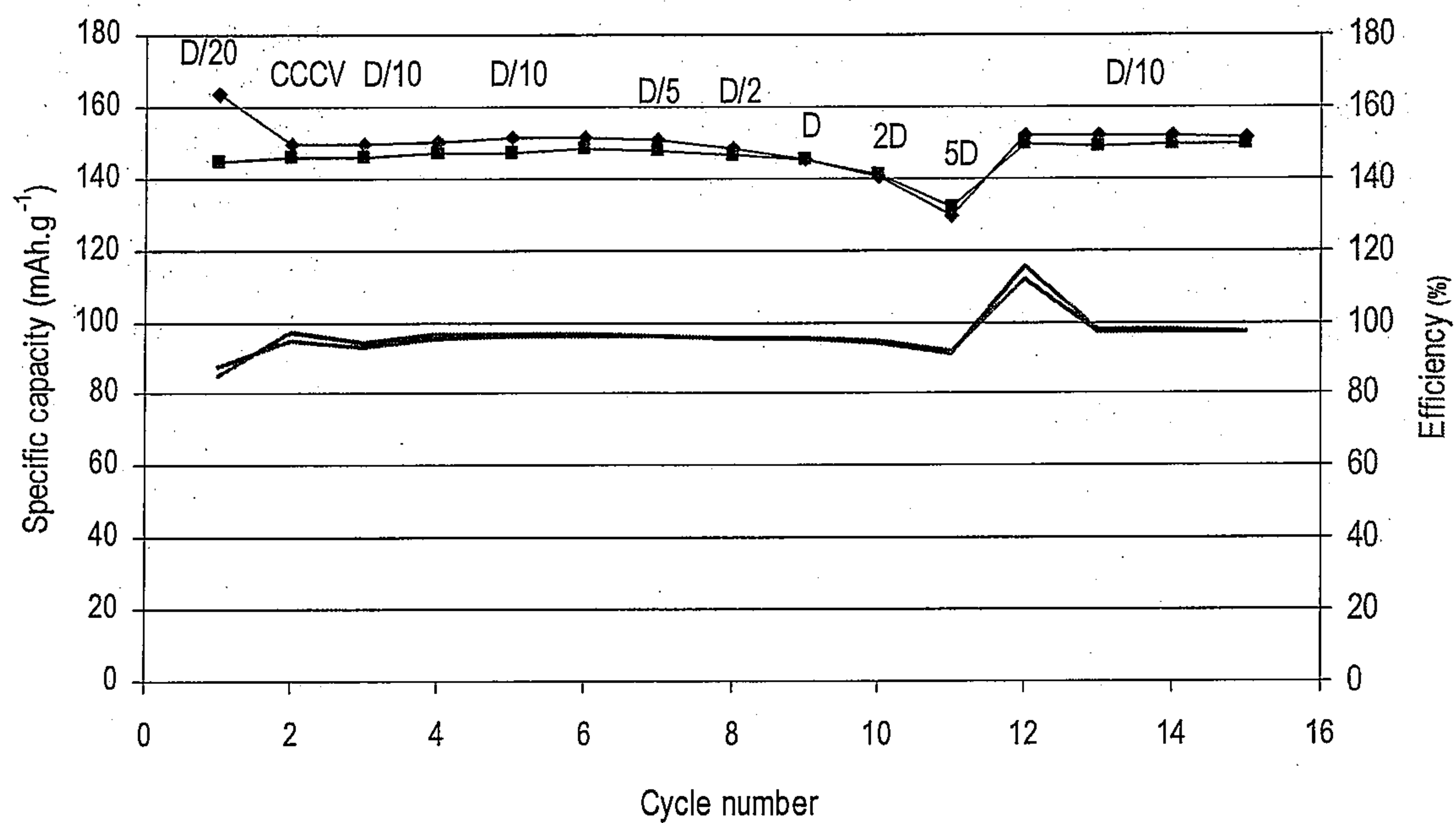


Figure 3

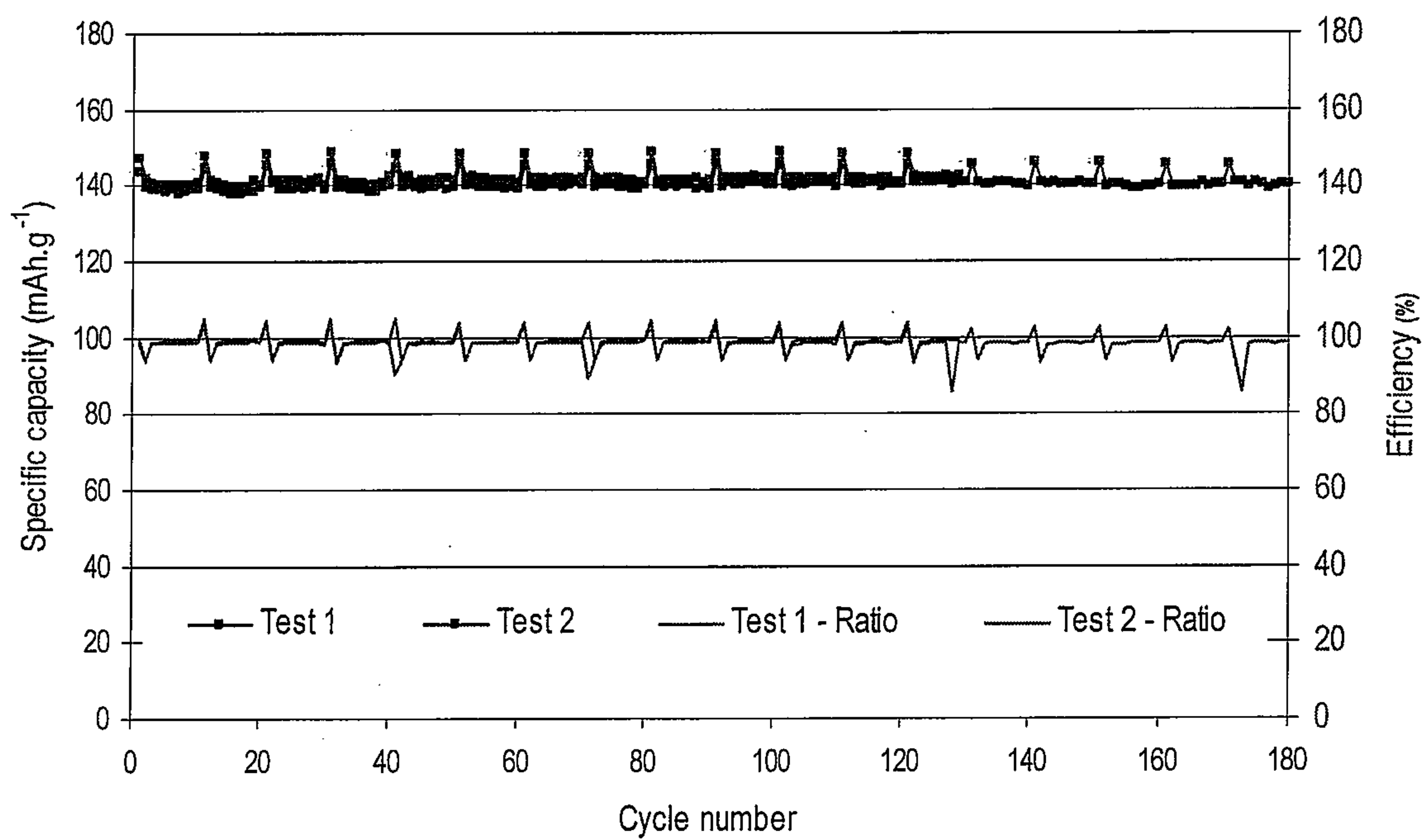


Figure 4

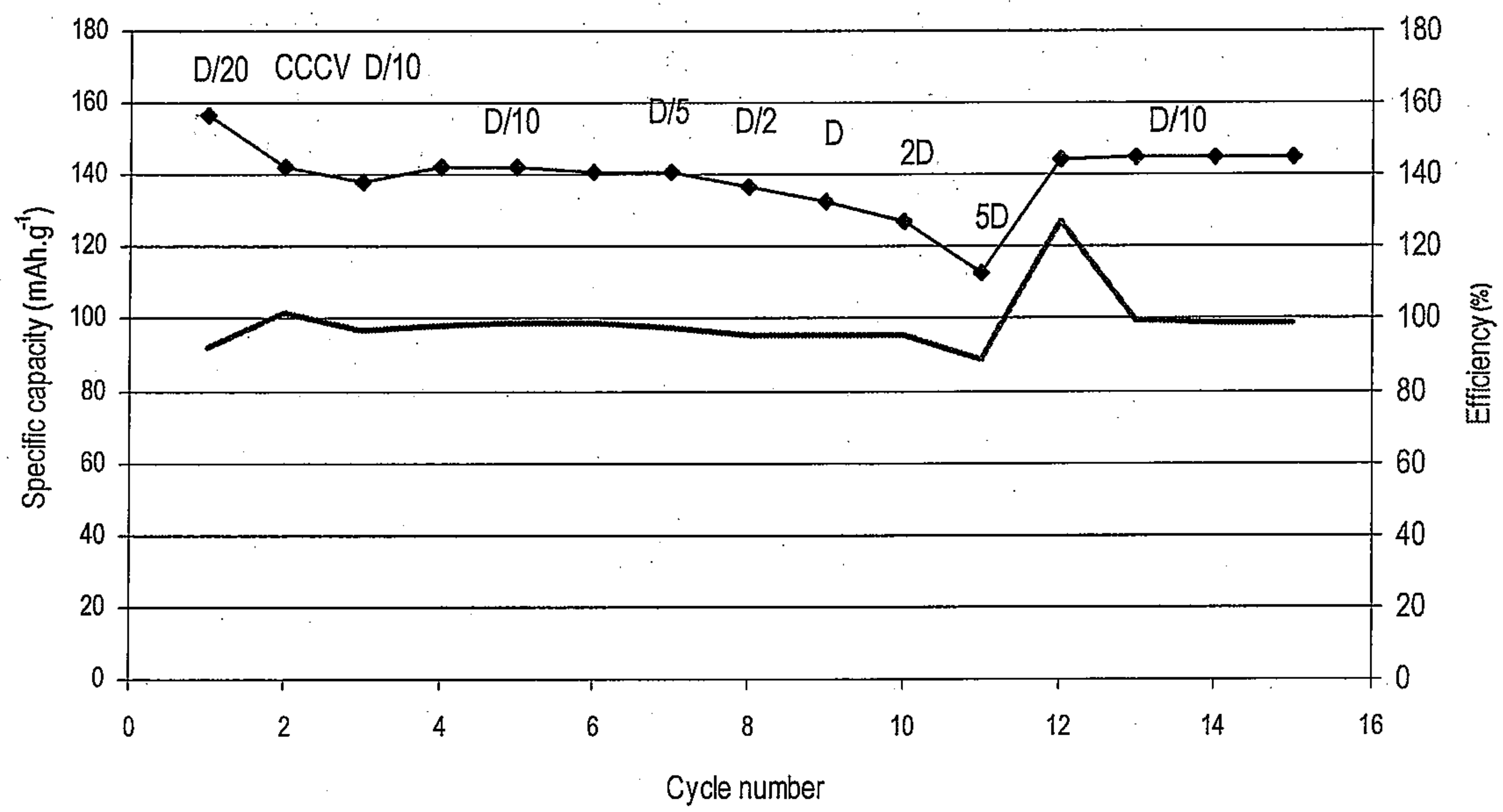


Figure 5

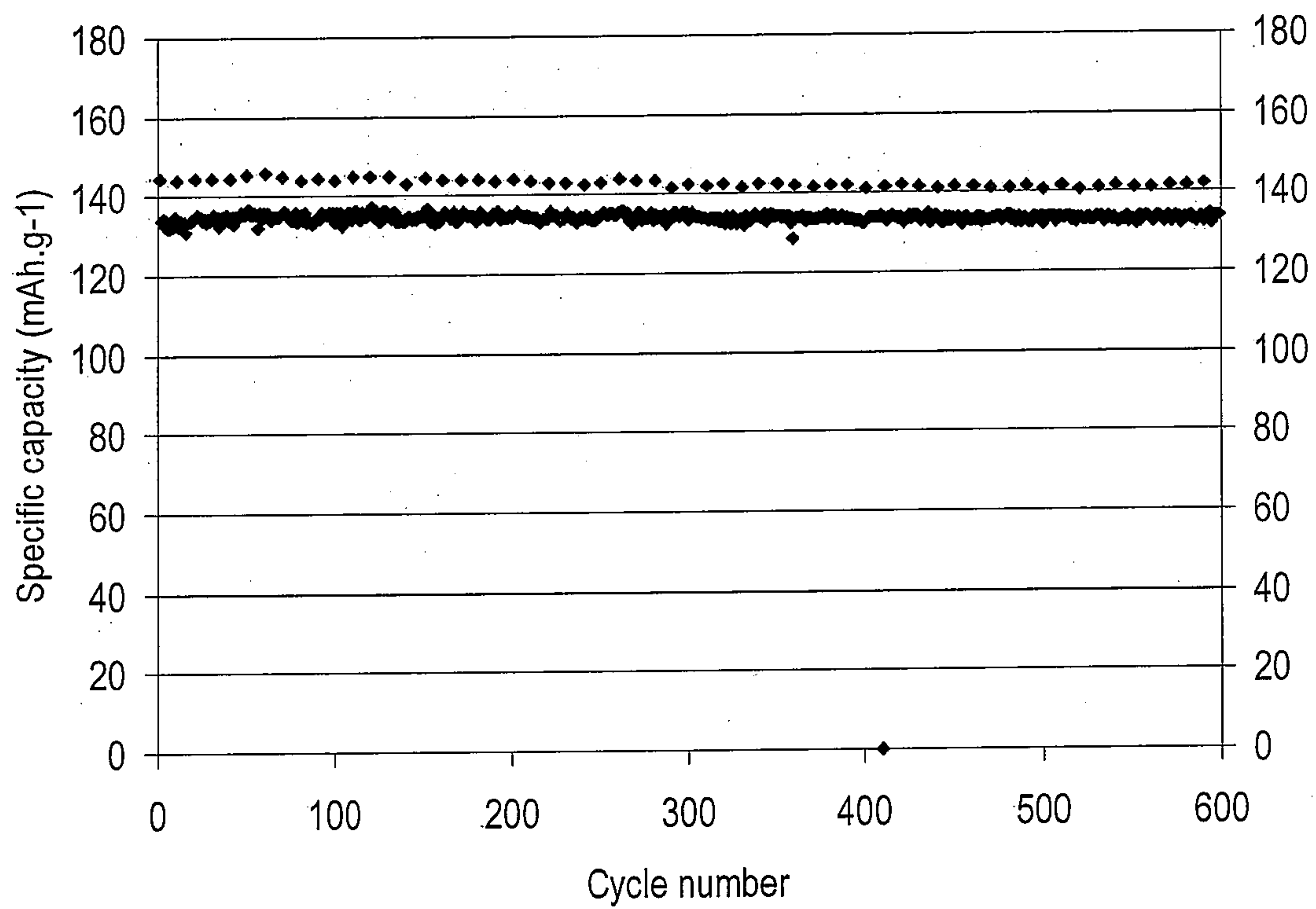


Figure 6a

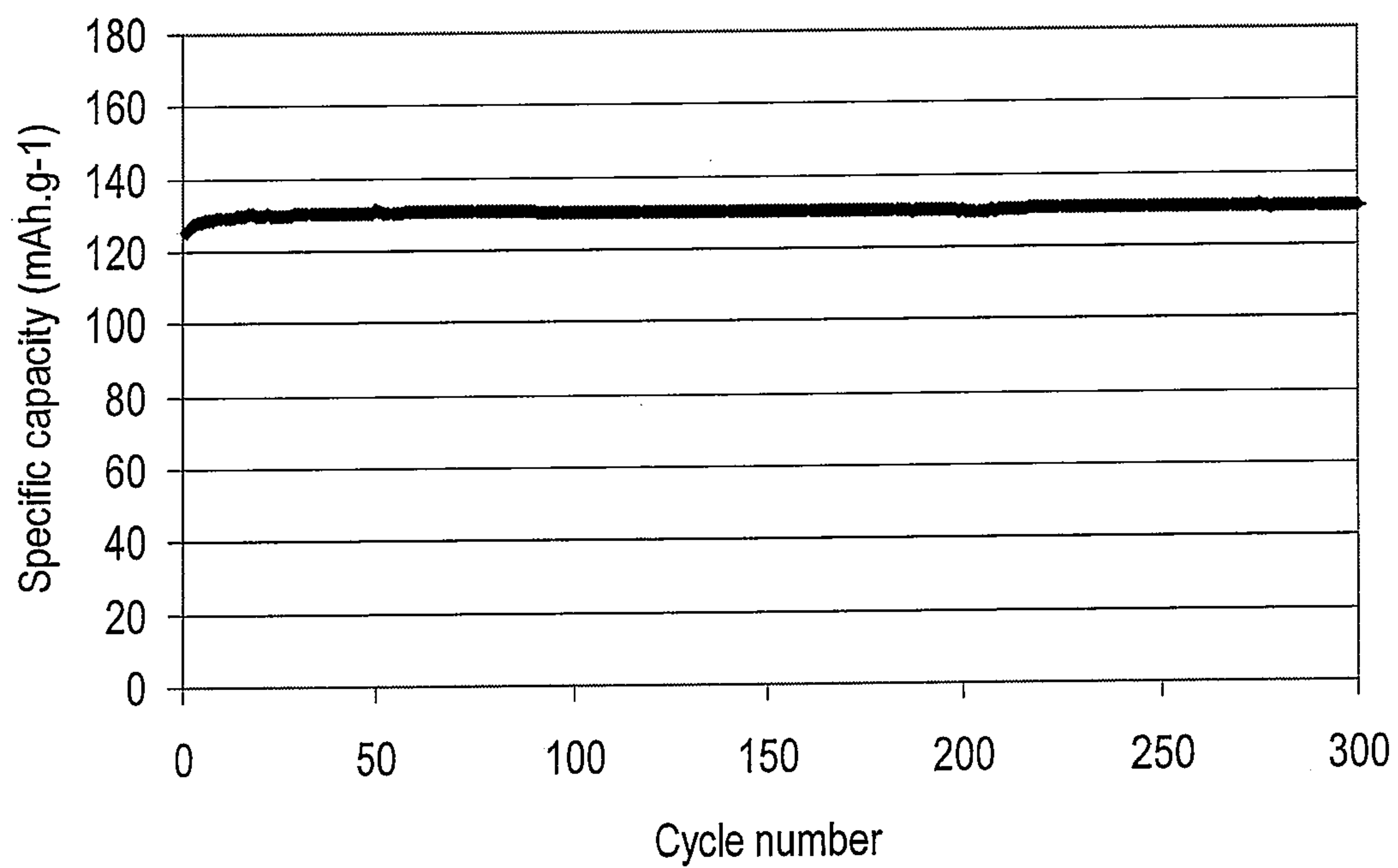


Figure 6b

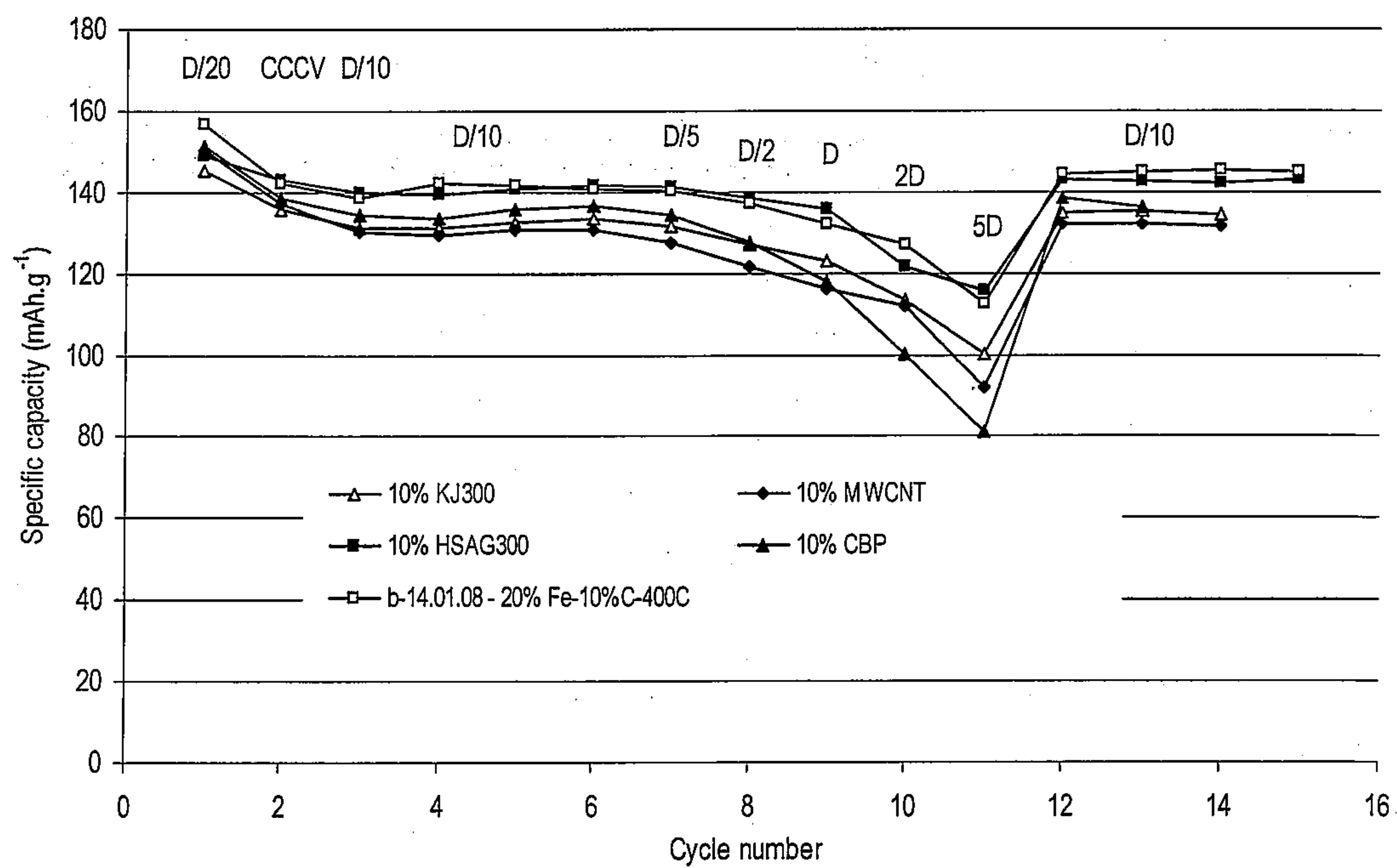


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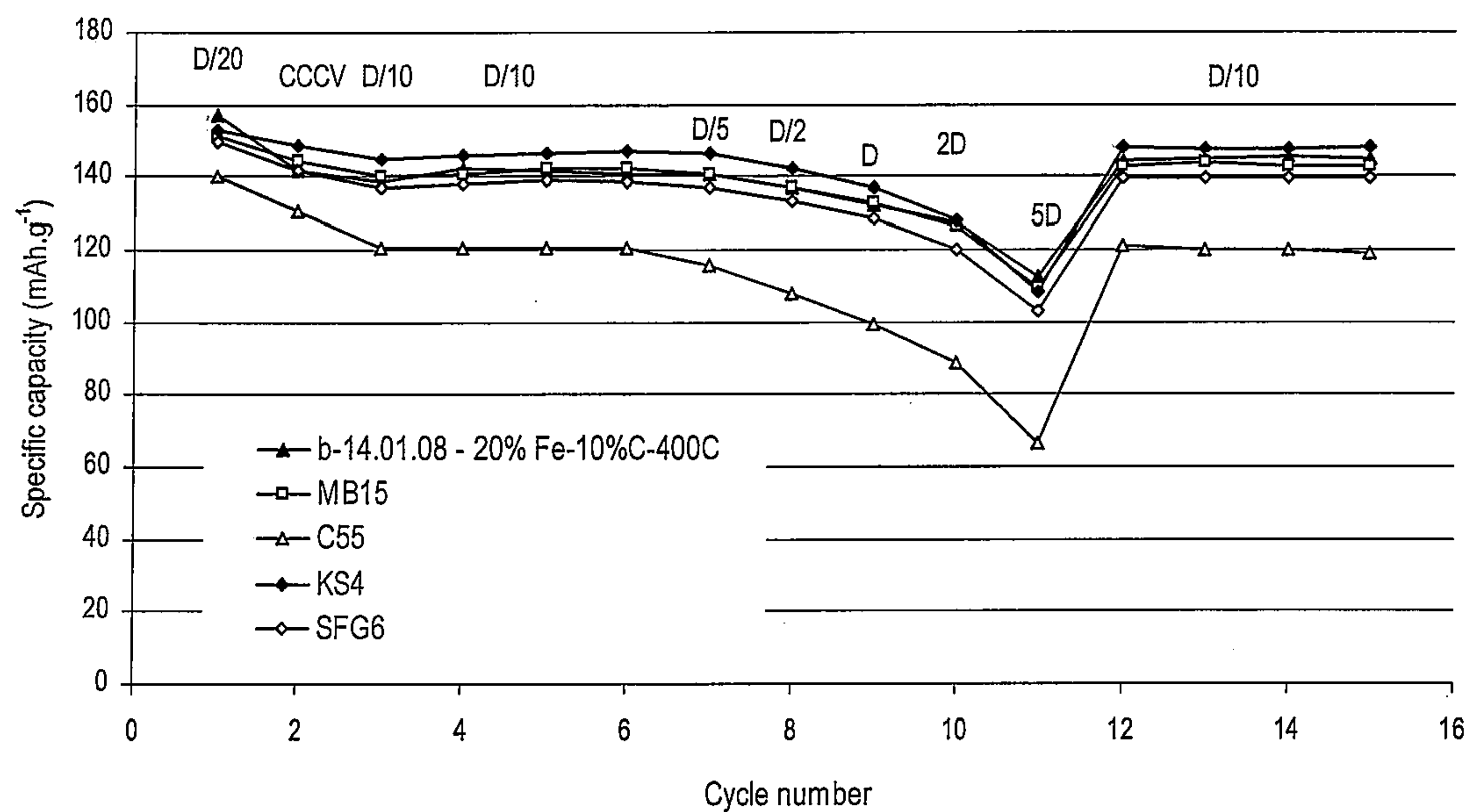


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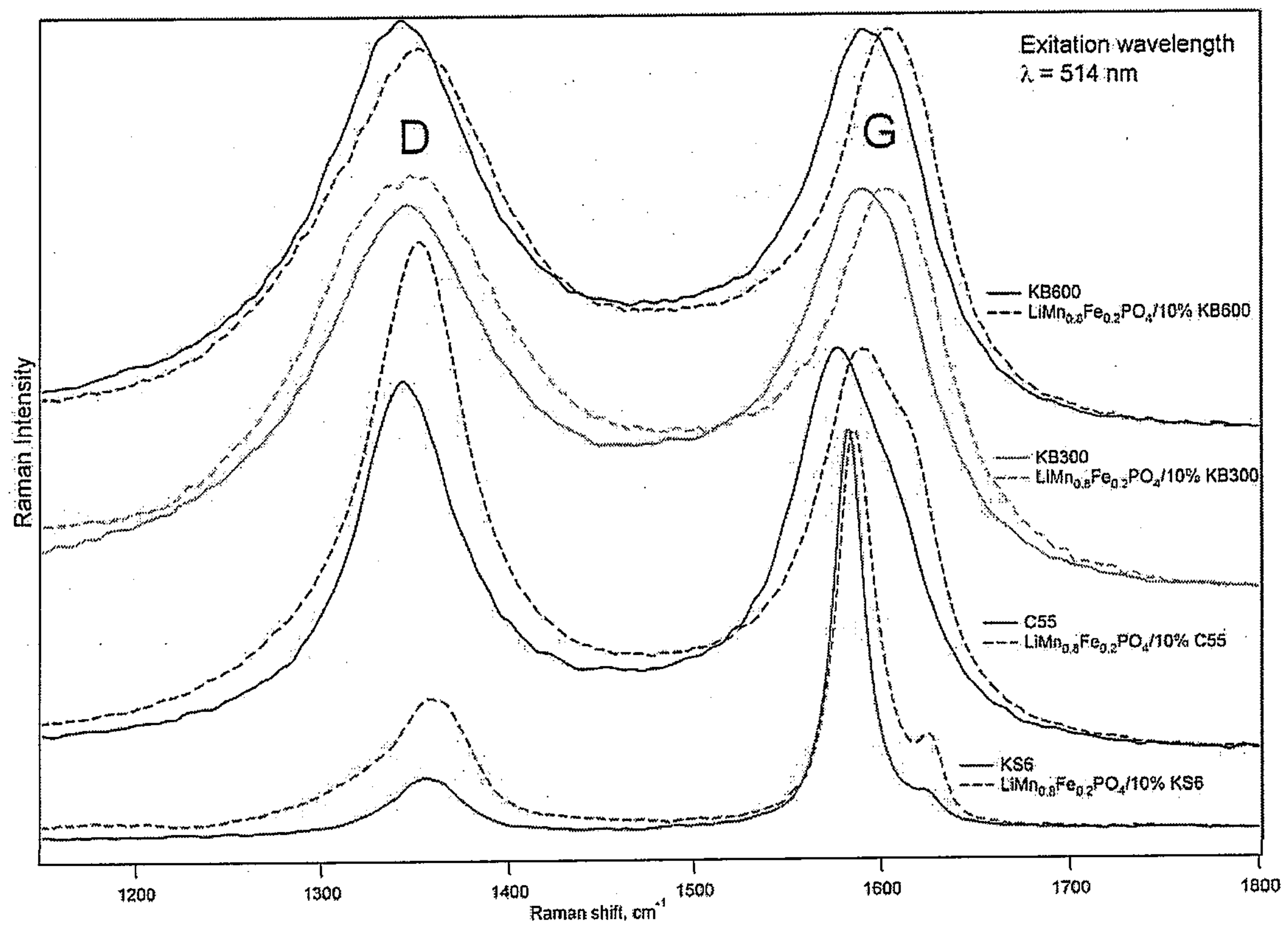


Figure 9

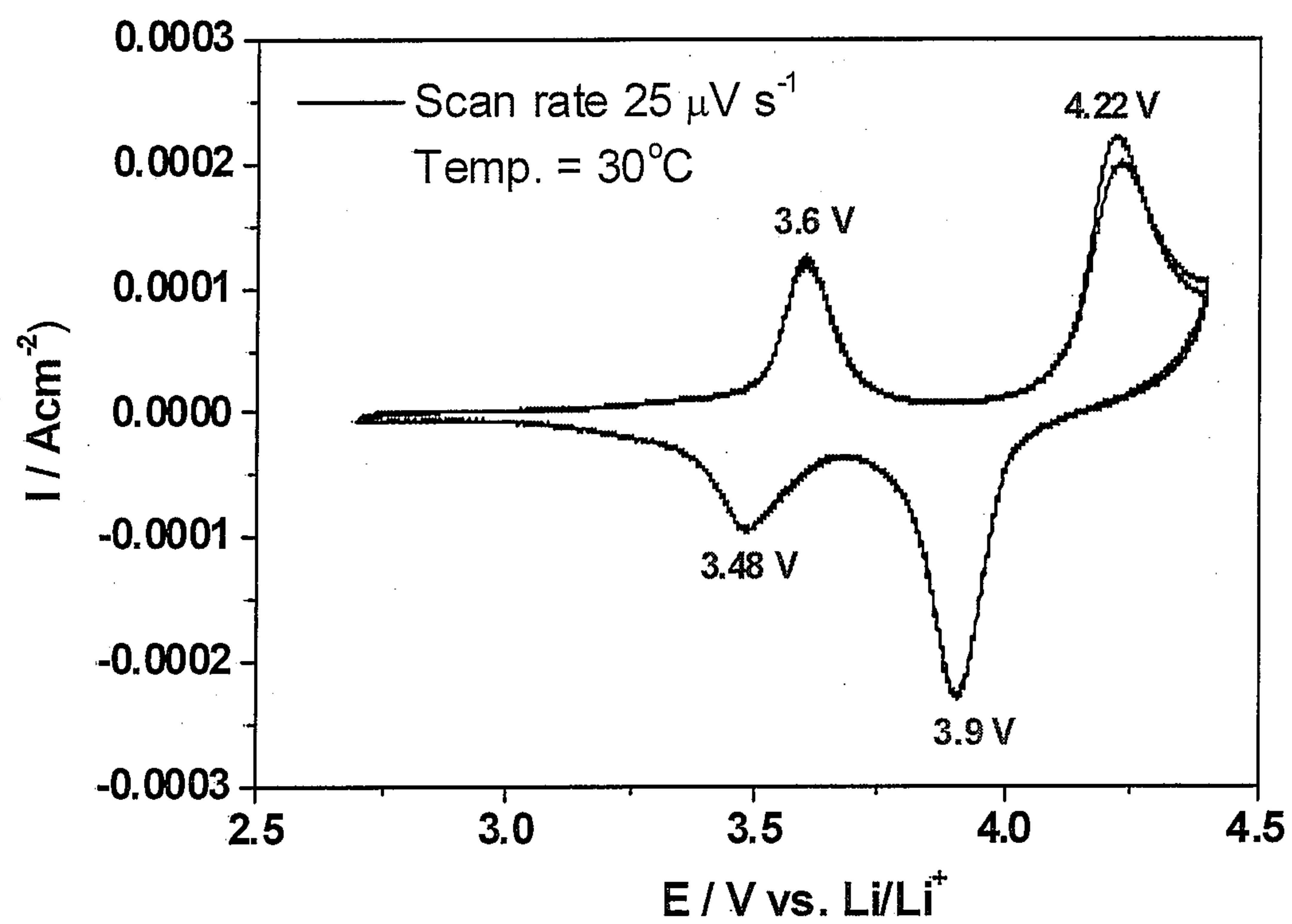


Figure 10

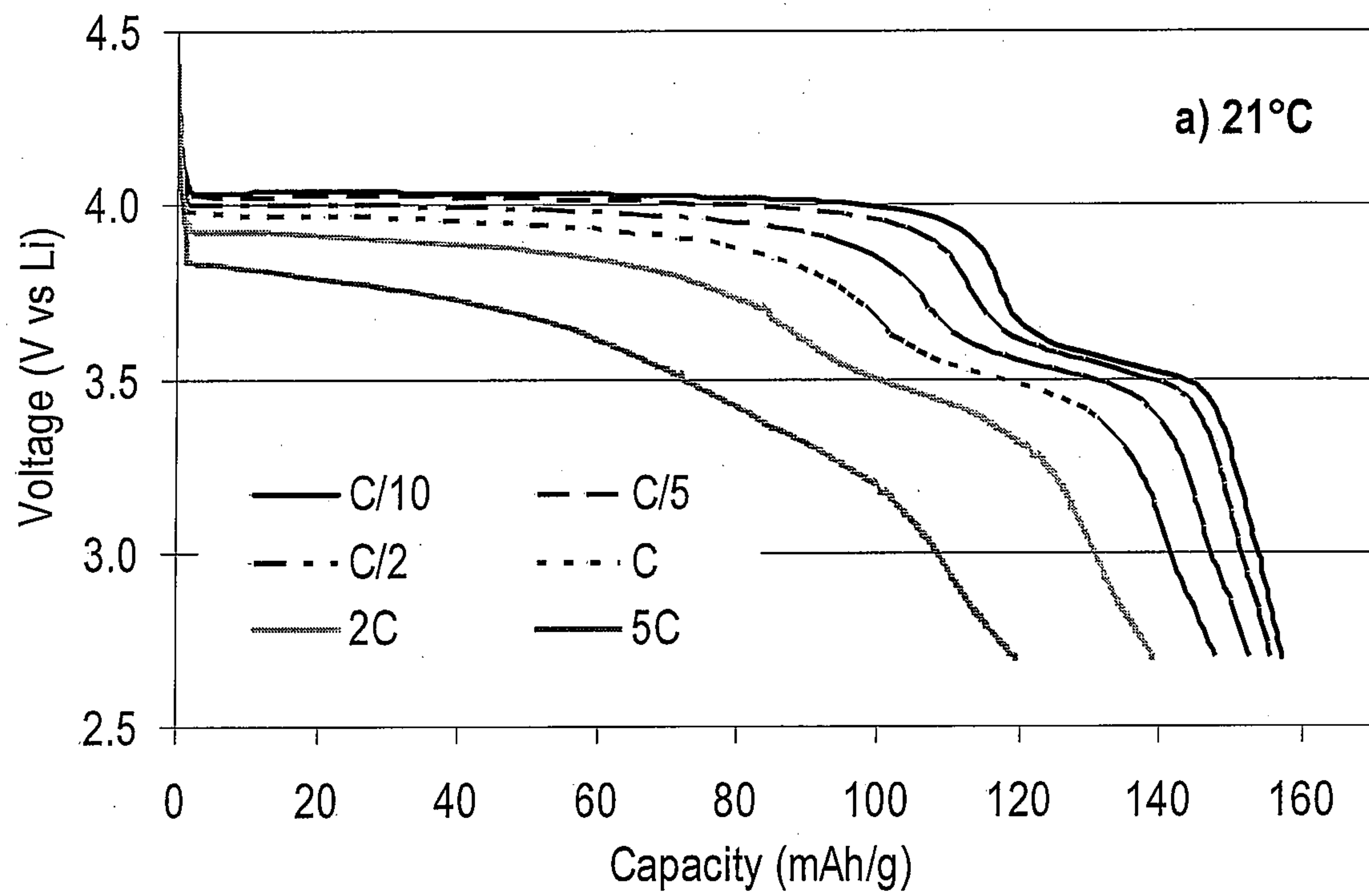


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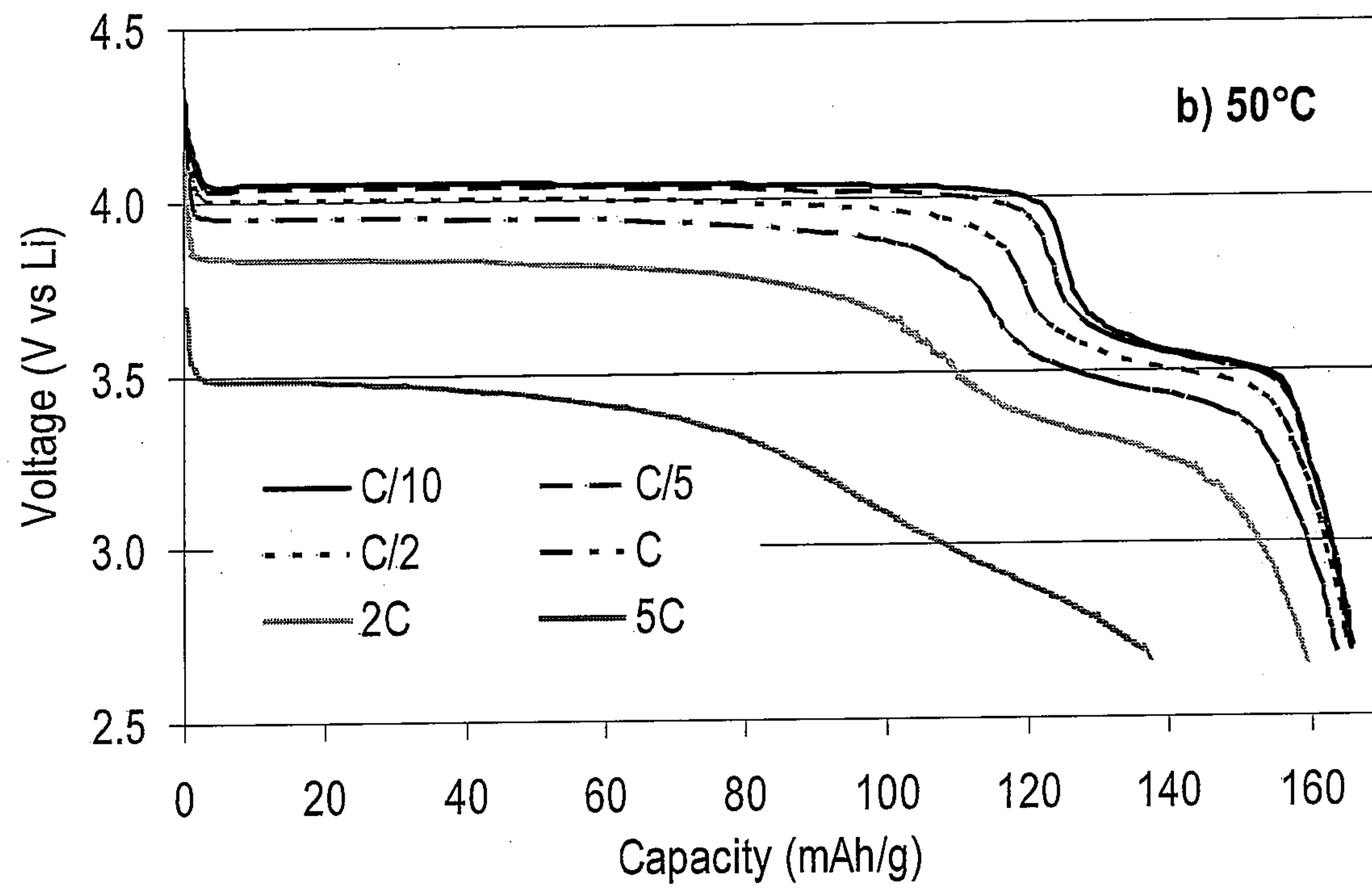


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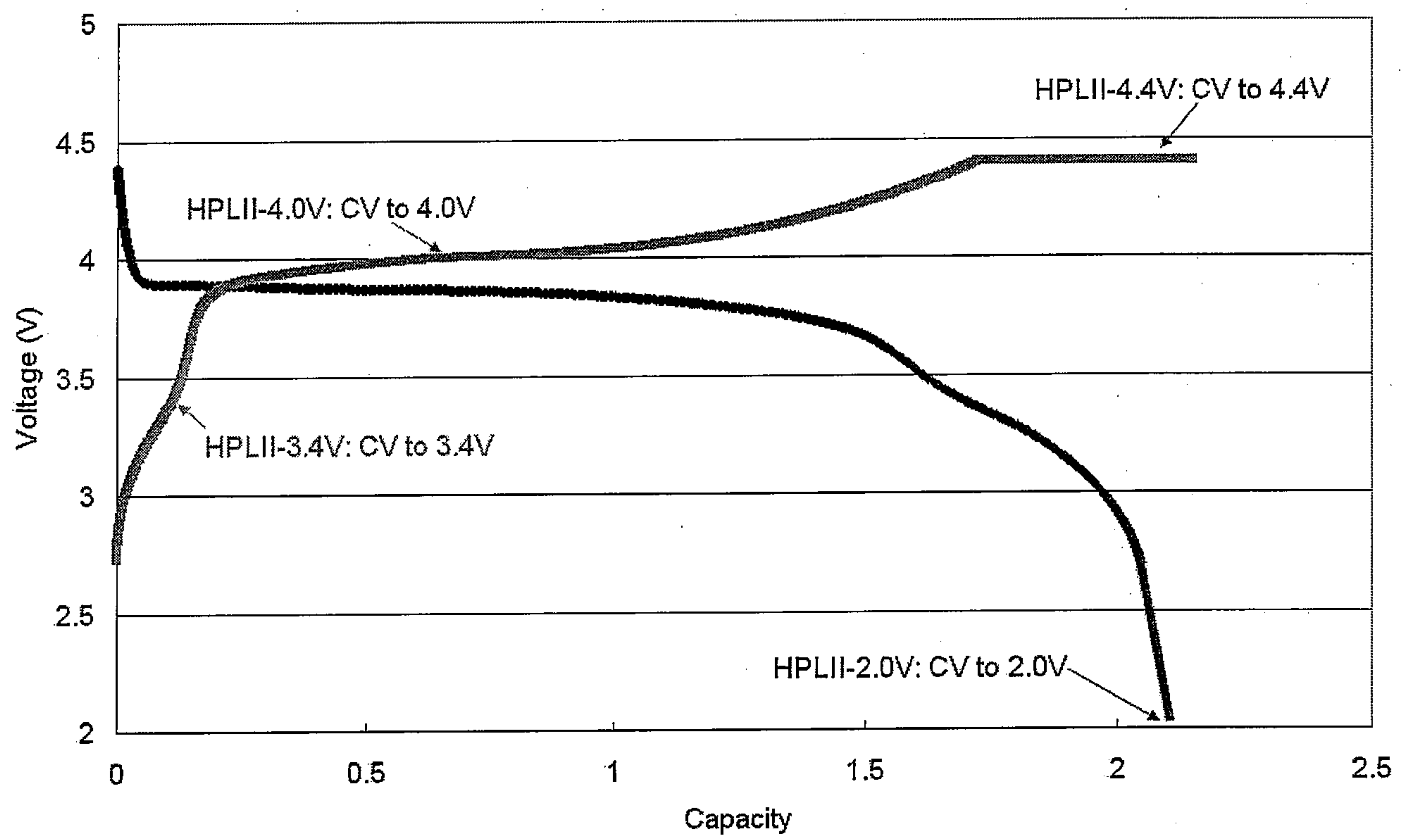
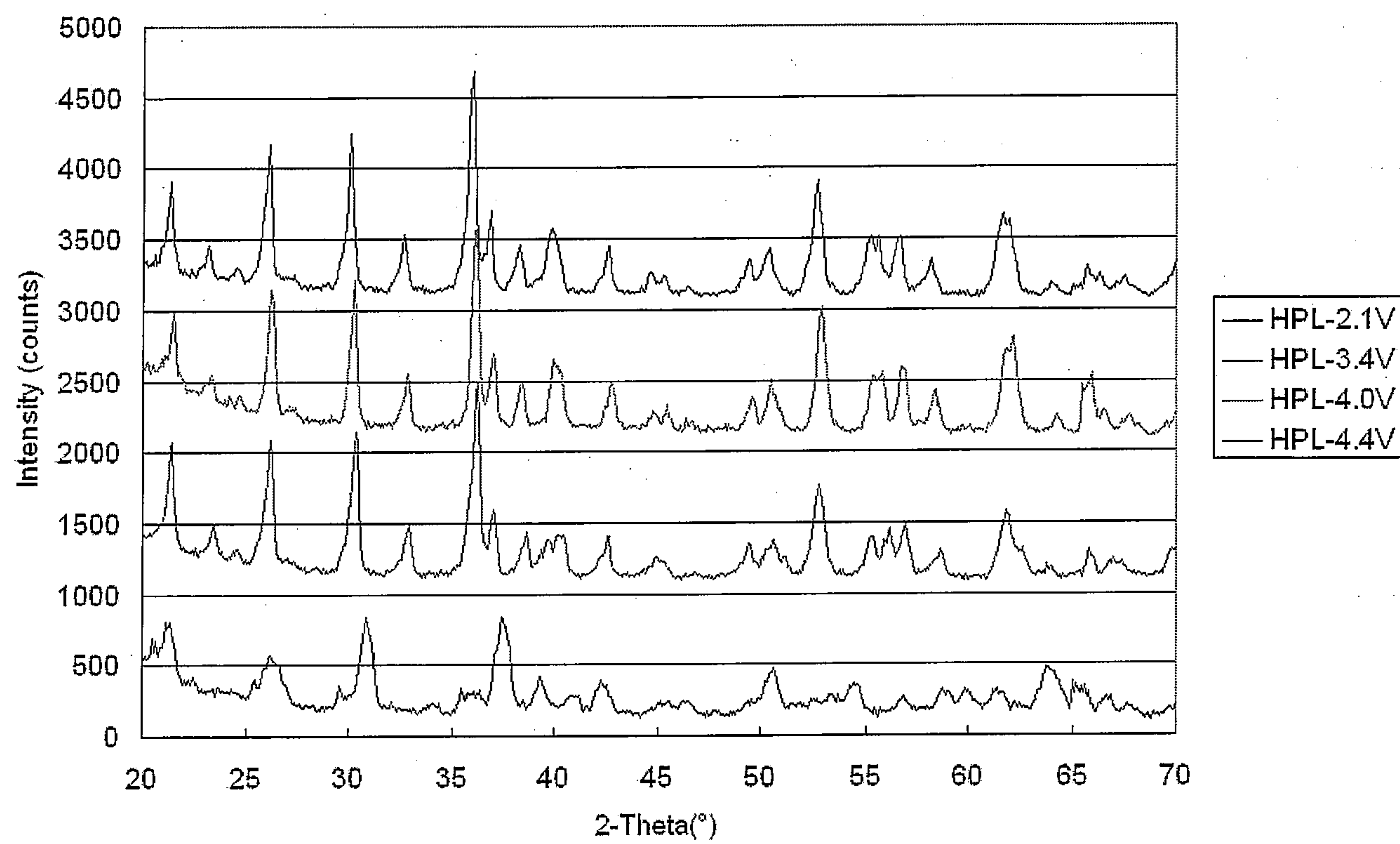
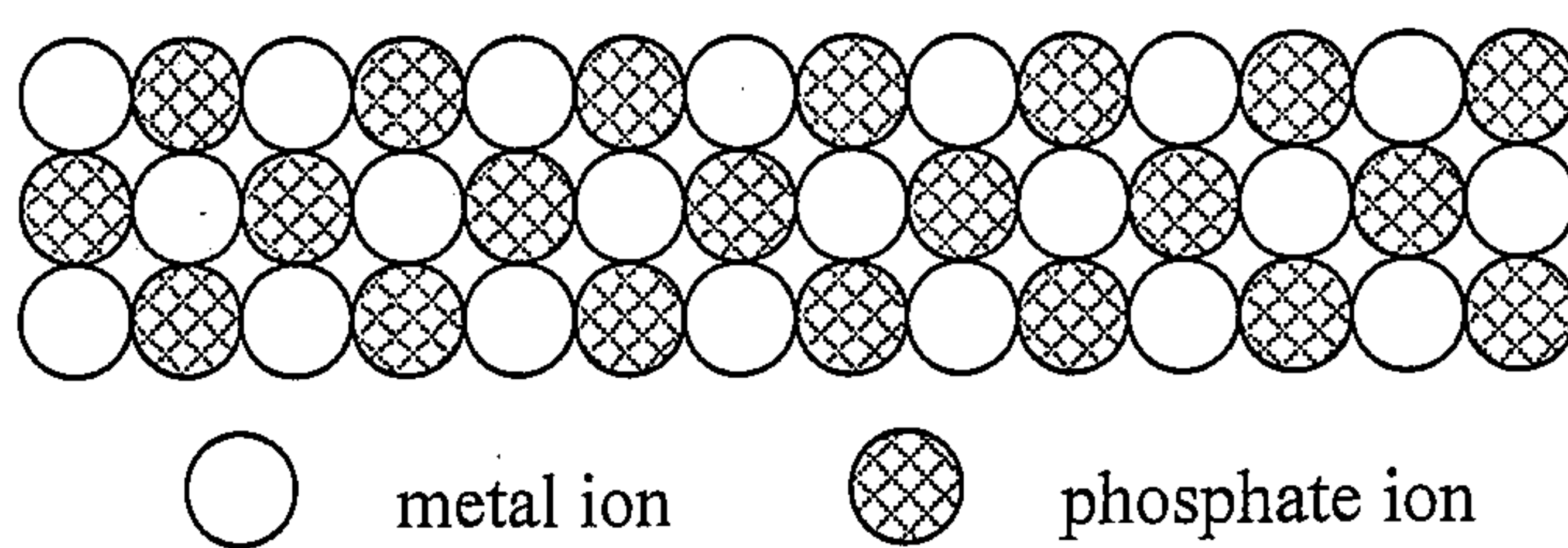


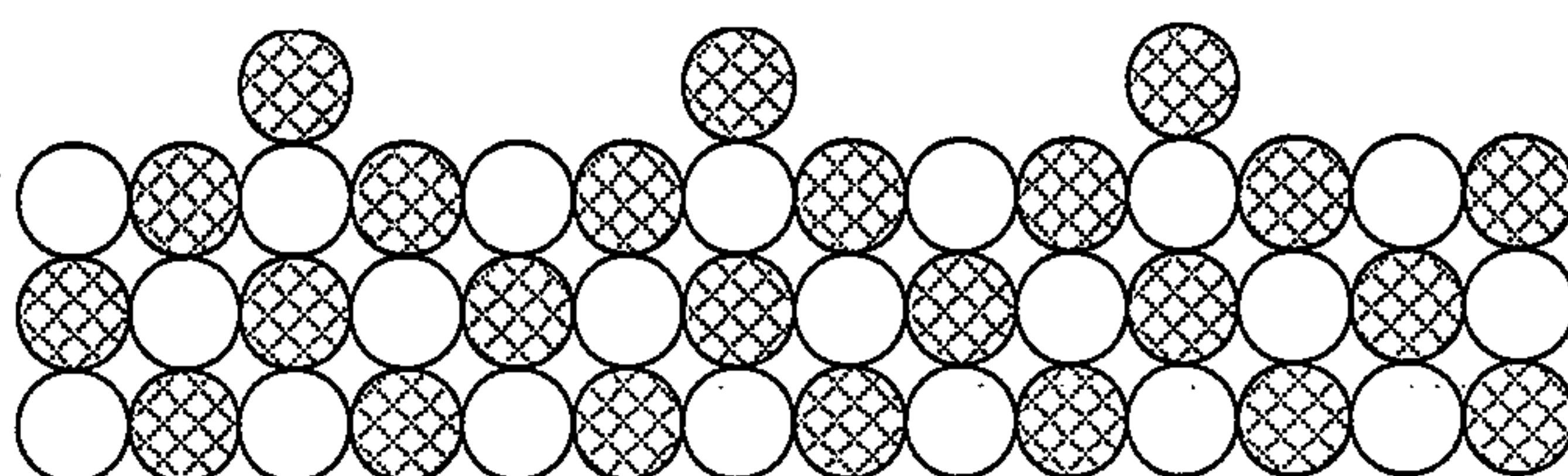
Figure 13

**Figure 14**

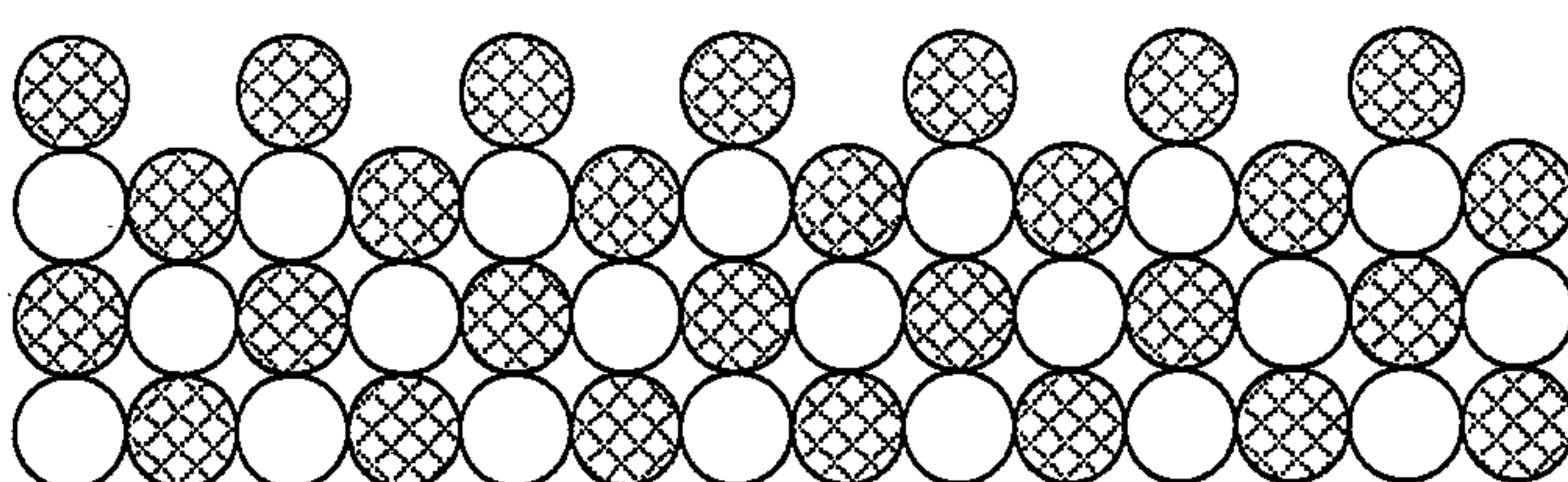
a) stoichiometric surface



b) partially phosphate terminated surface



c) fully phosphate terminated surface



d) partially diphosphate terminated surface

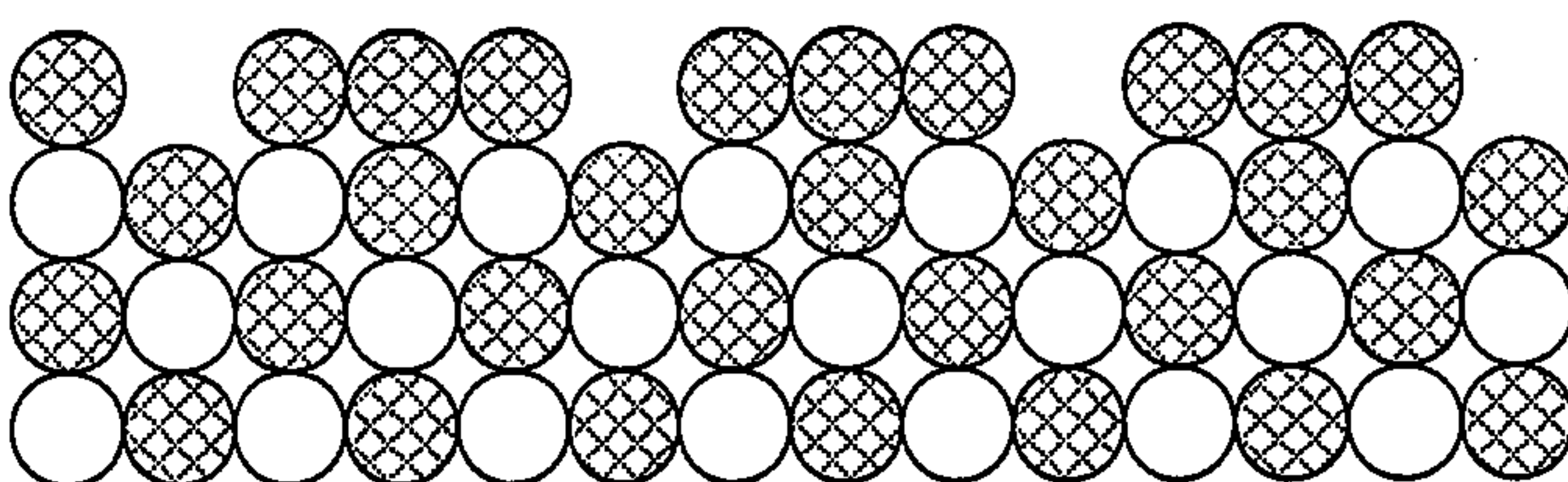
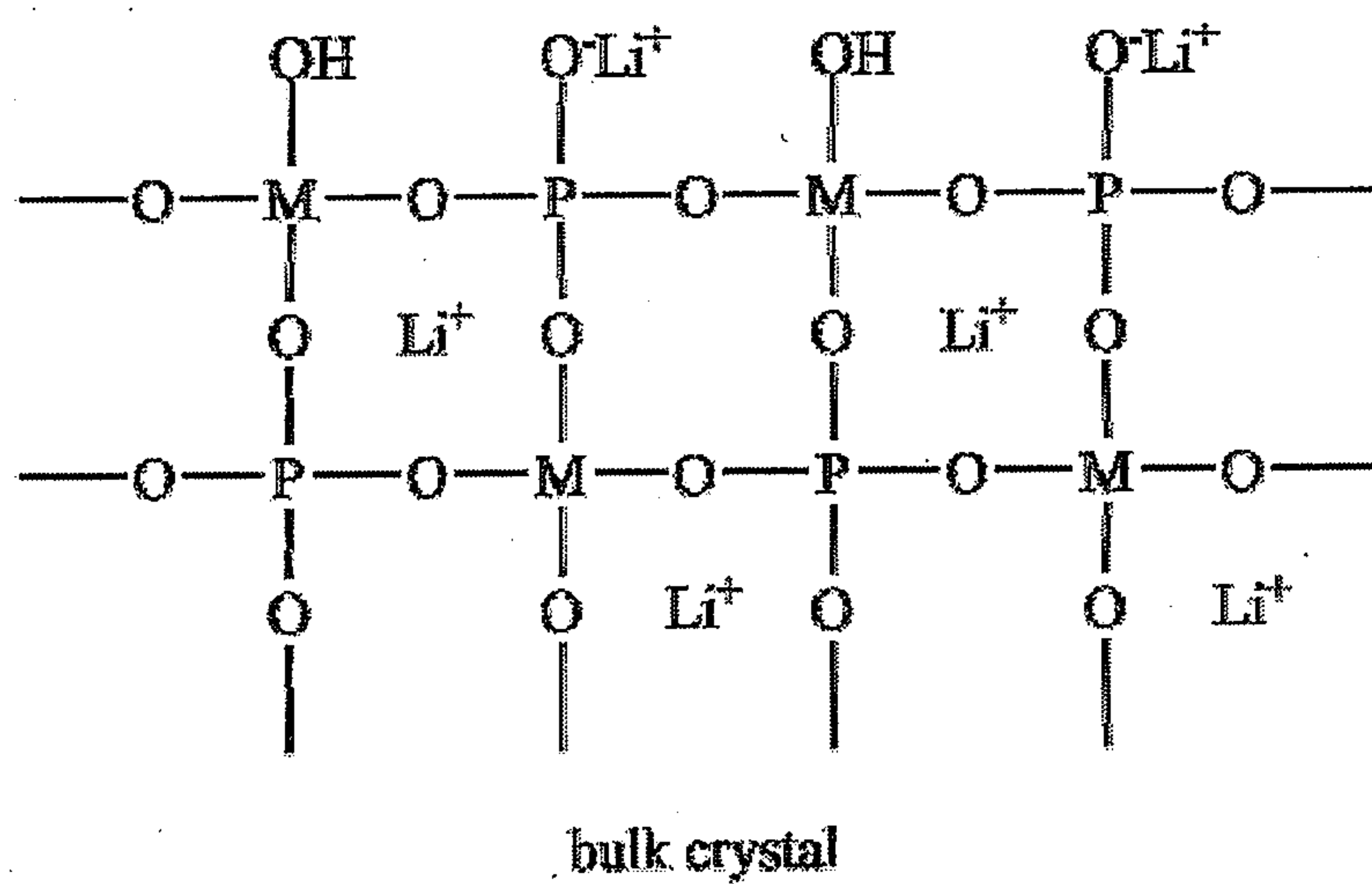


Figure 15

a) stoichiometric surface



b) phosphate terminated surface

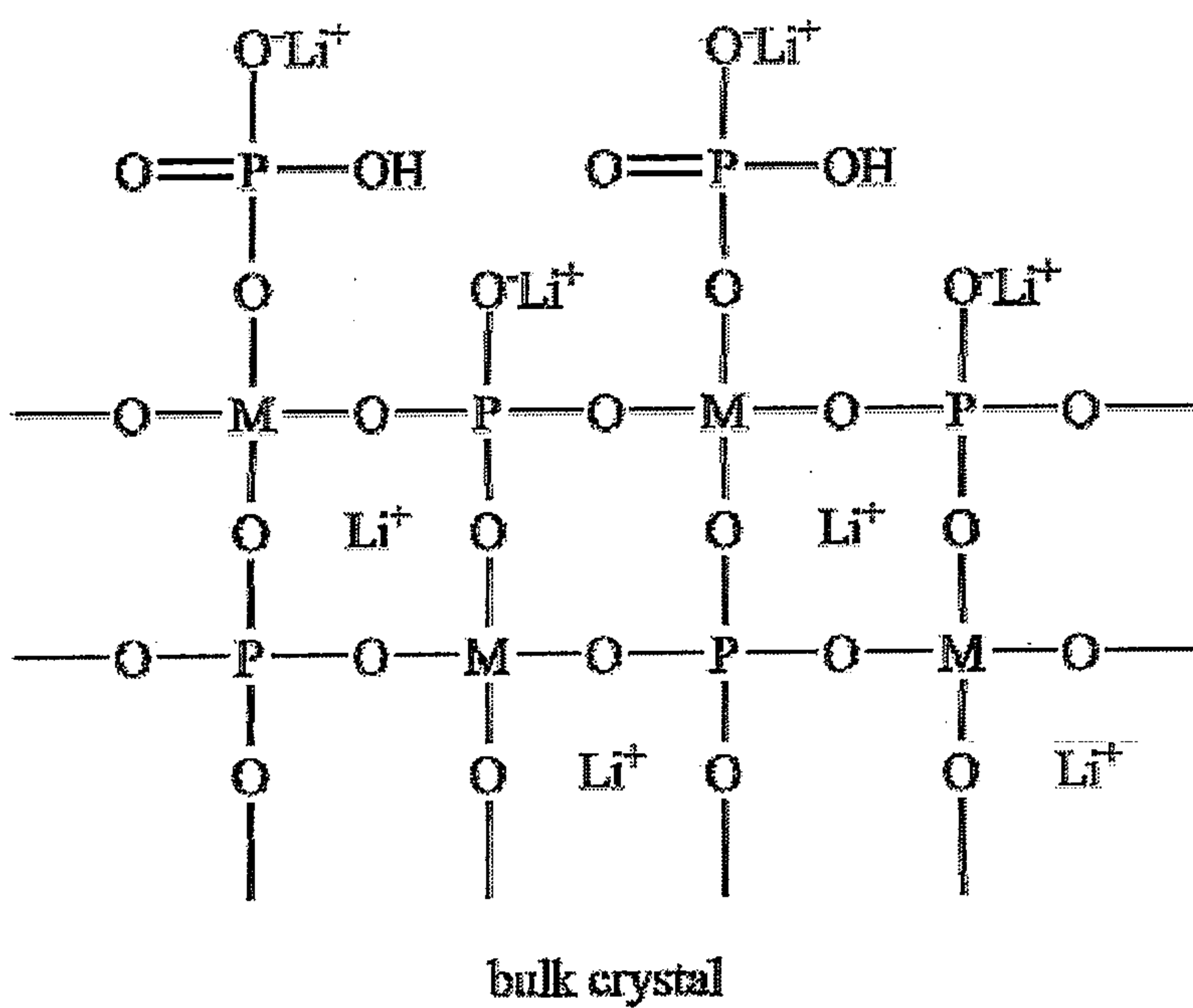
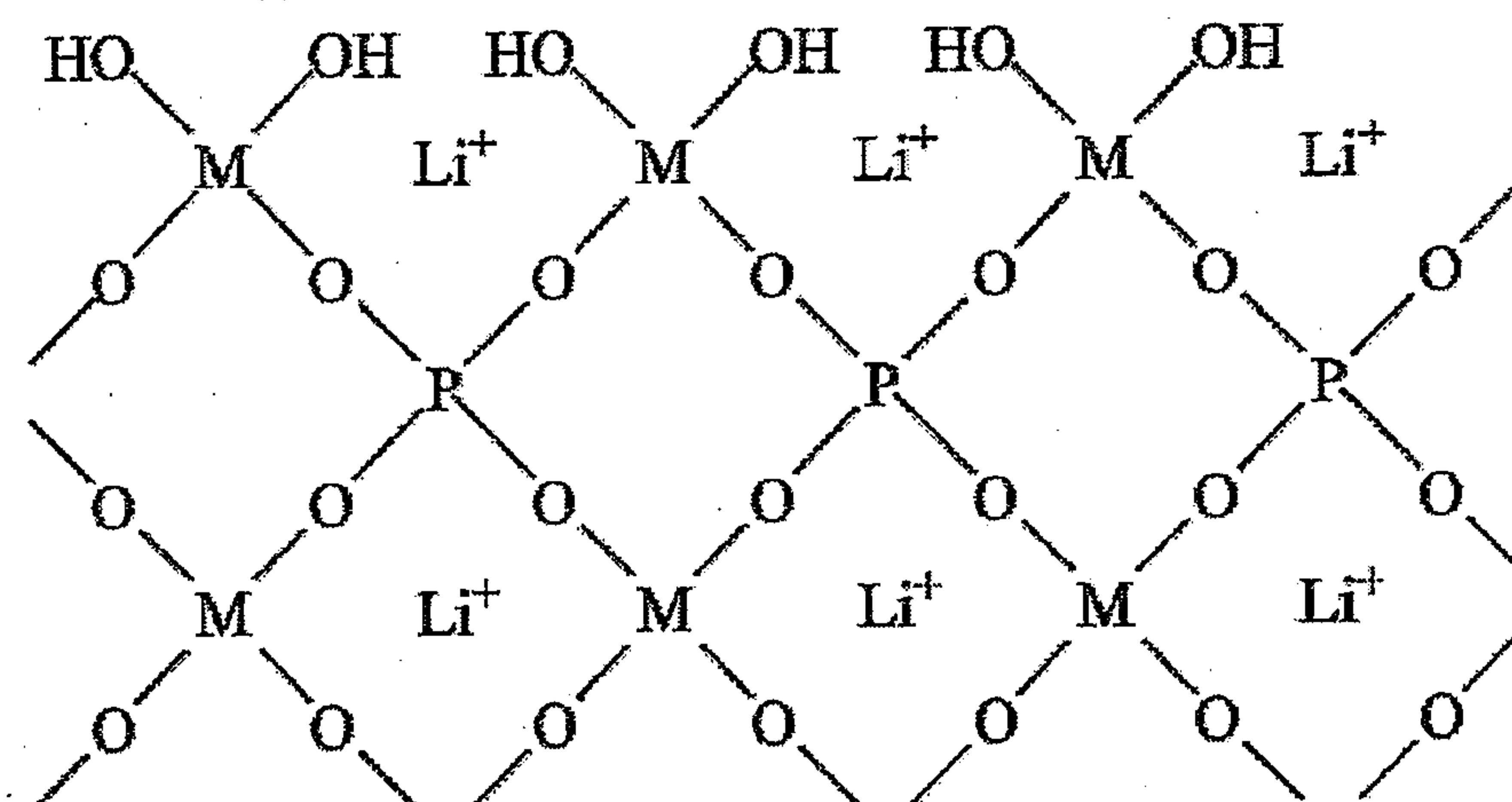


Figure 16

a) metal hydroxide terminated surface



b) phosphate terminated surface

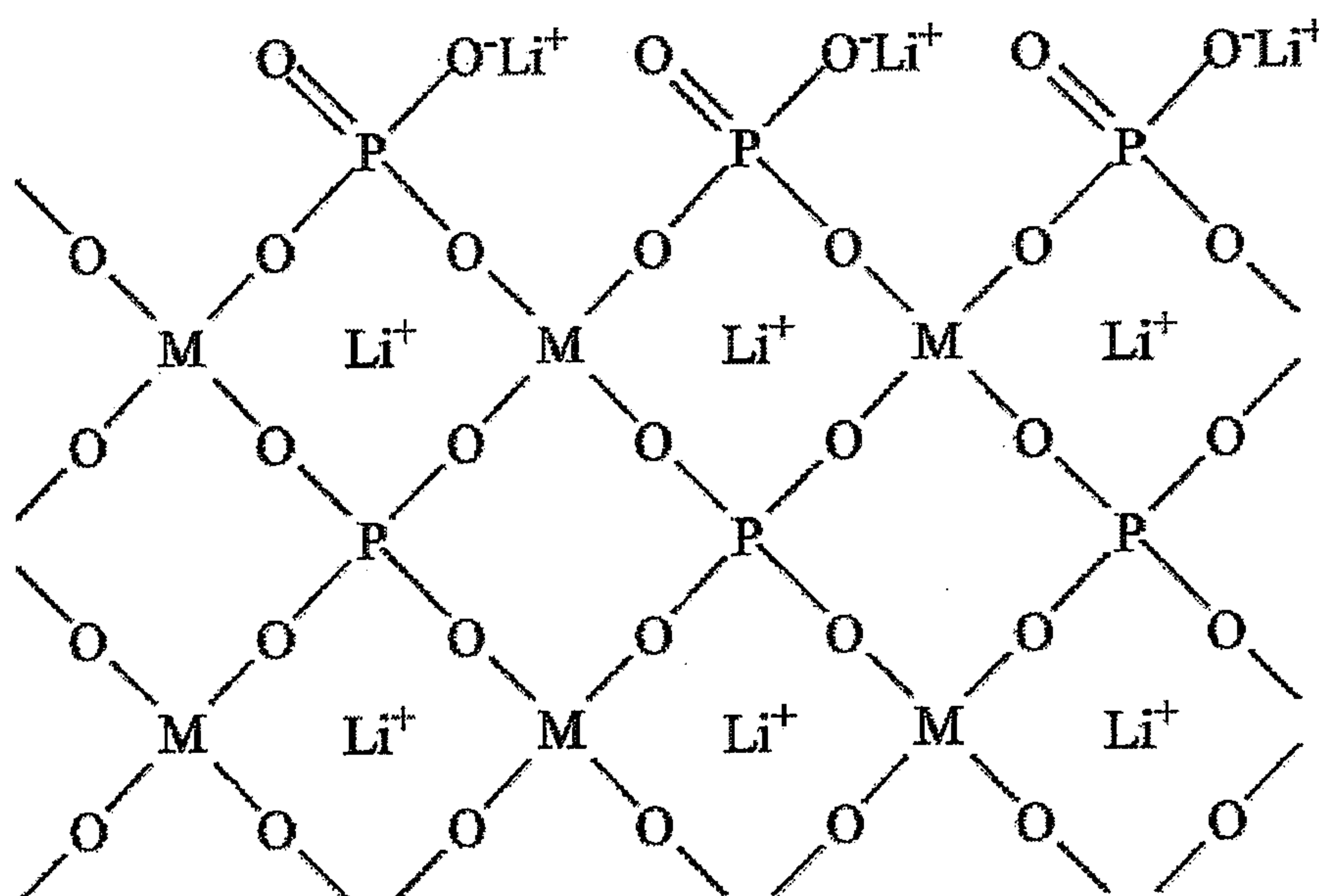


Figure 17

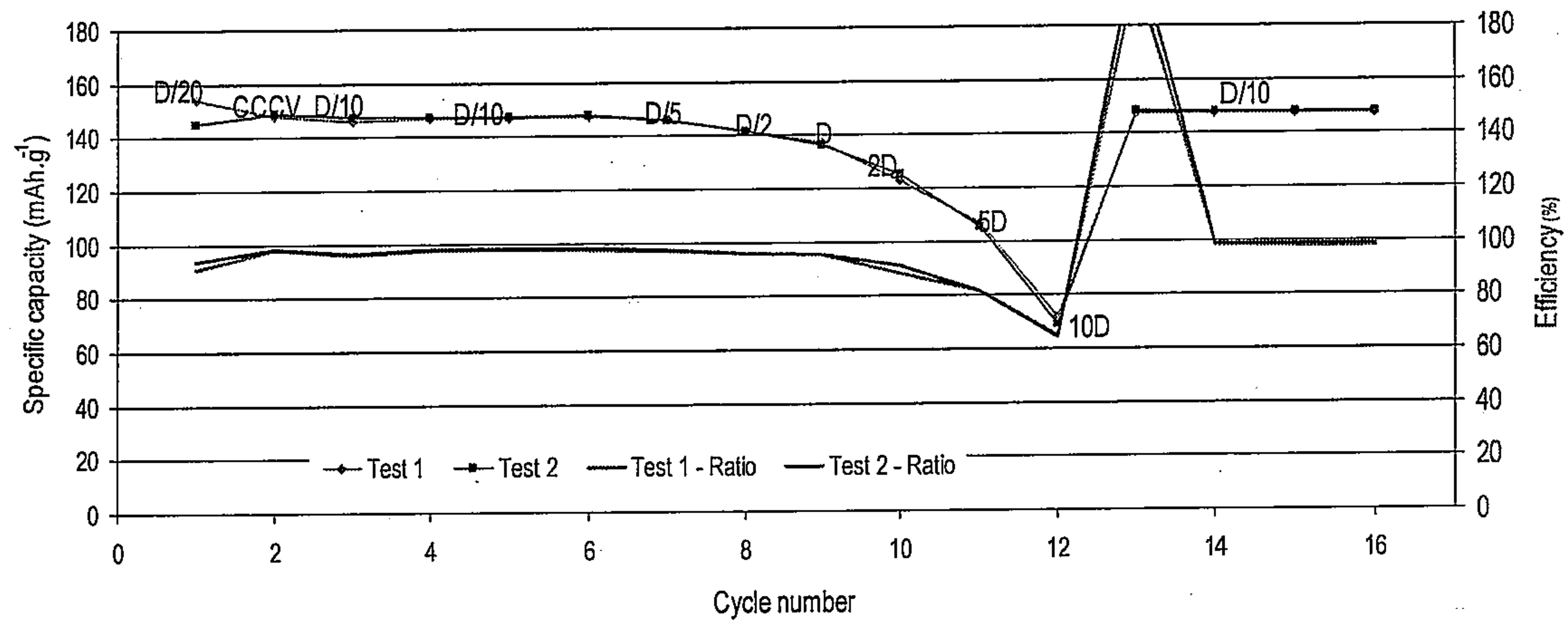


Figure 18

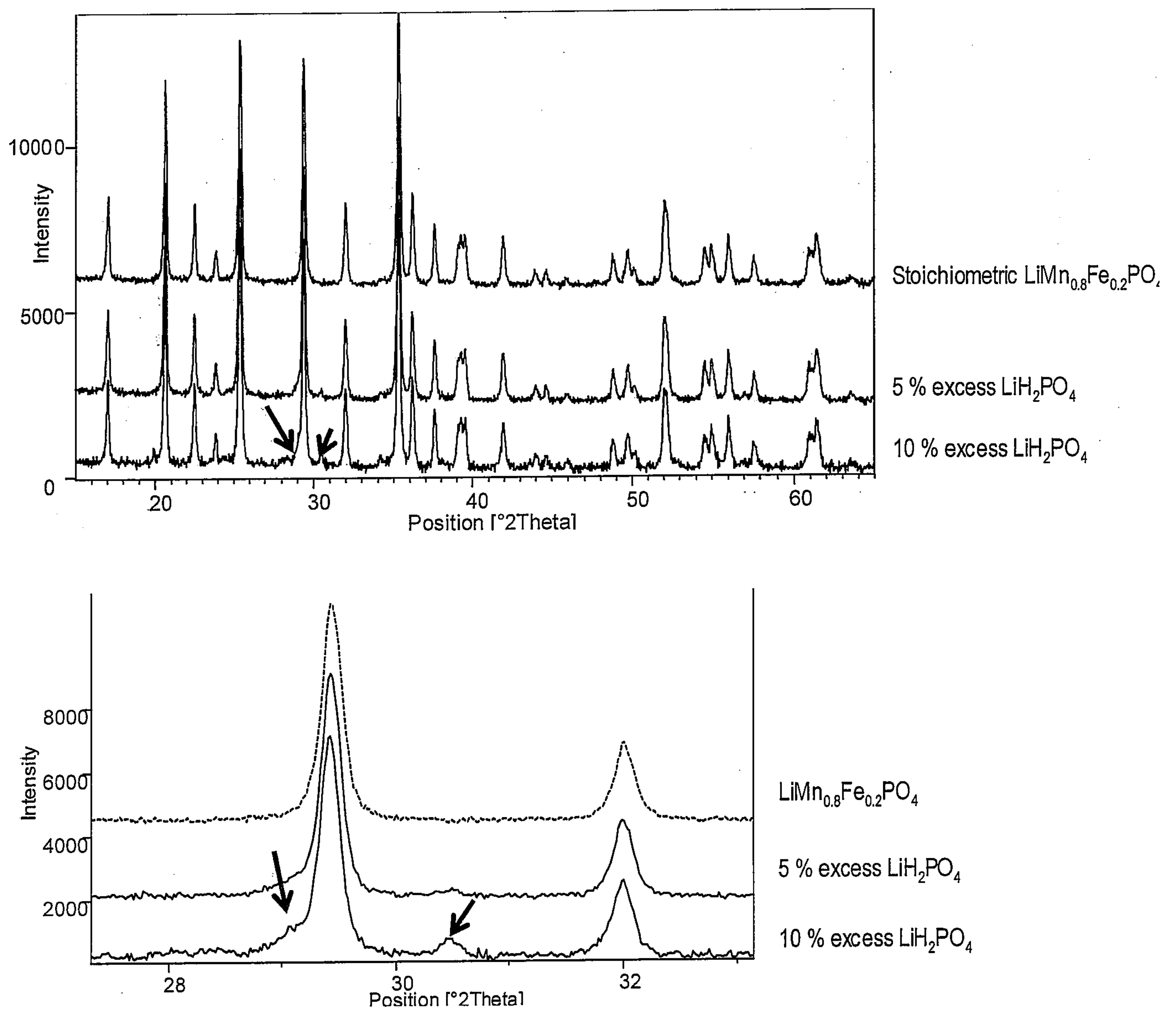
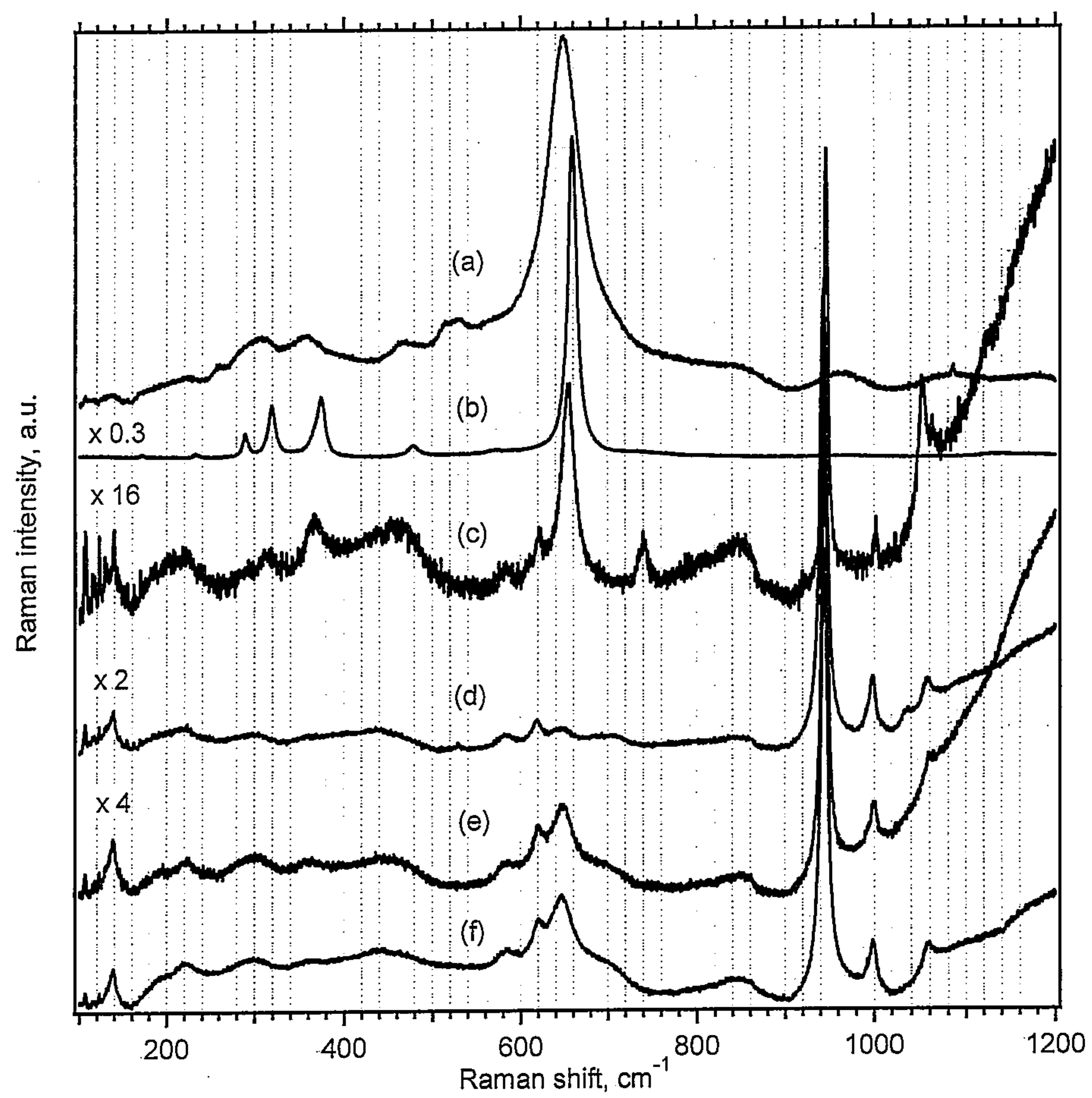
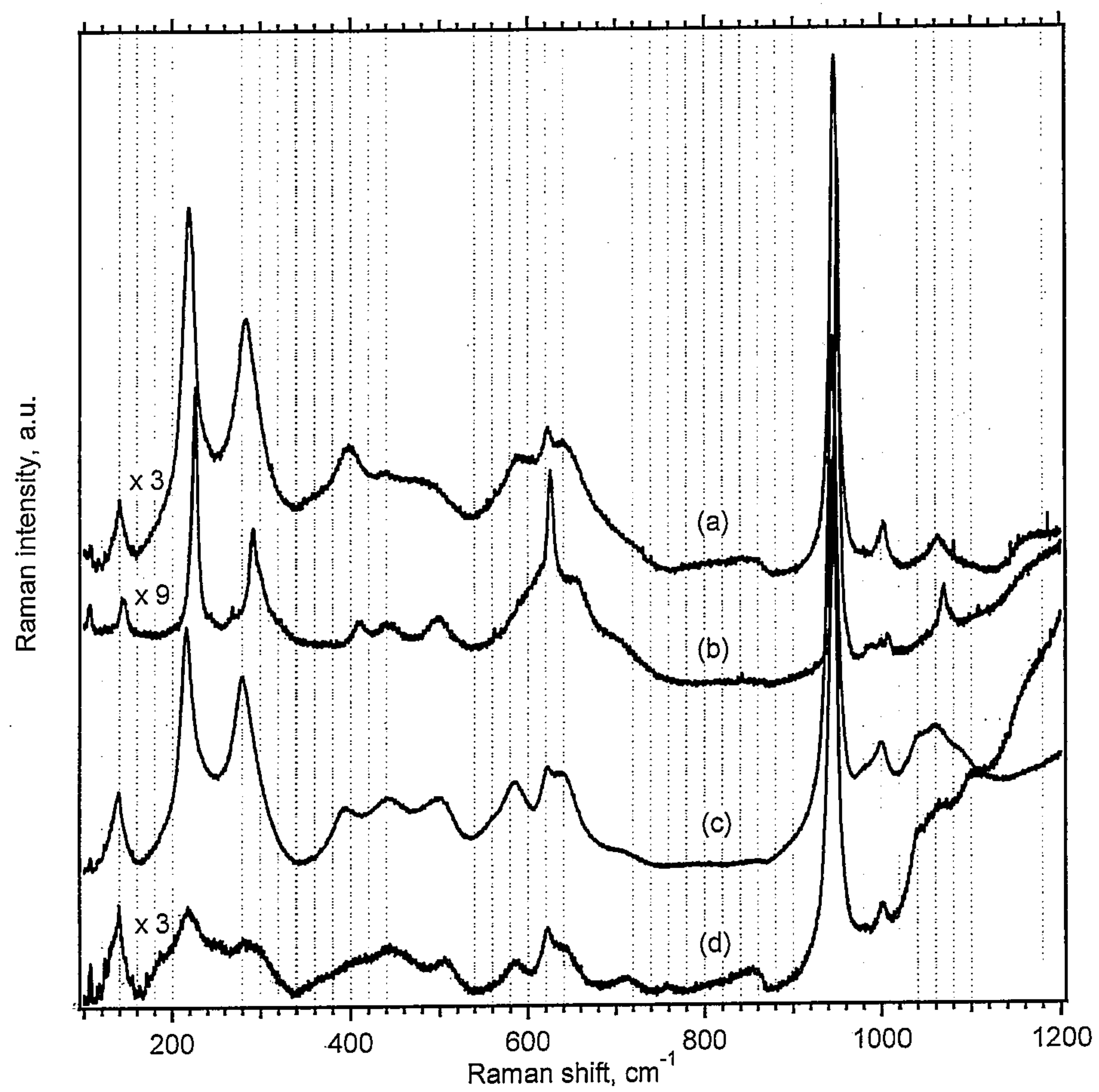
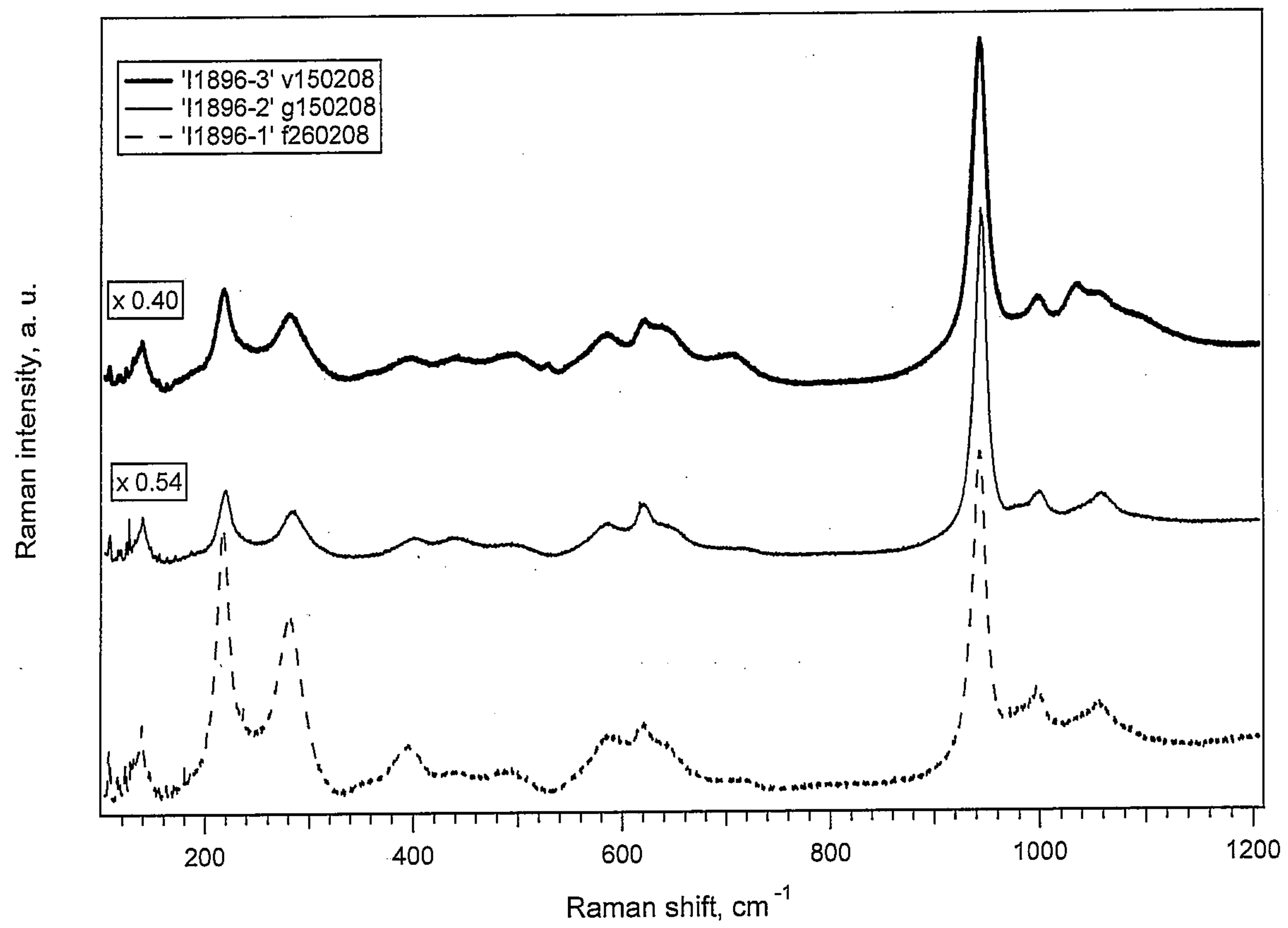


Figure 19

**Figure 20**

**Figure 21**

**Figure 22**

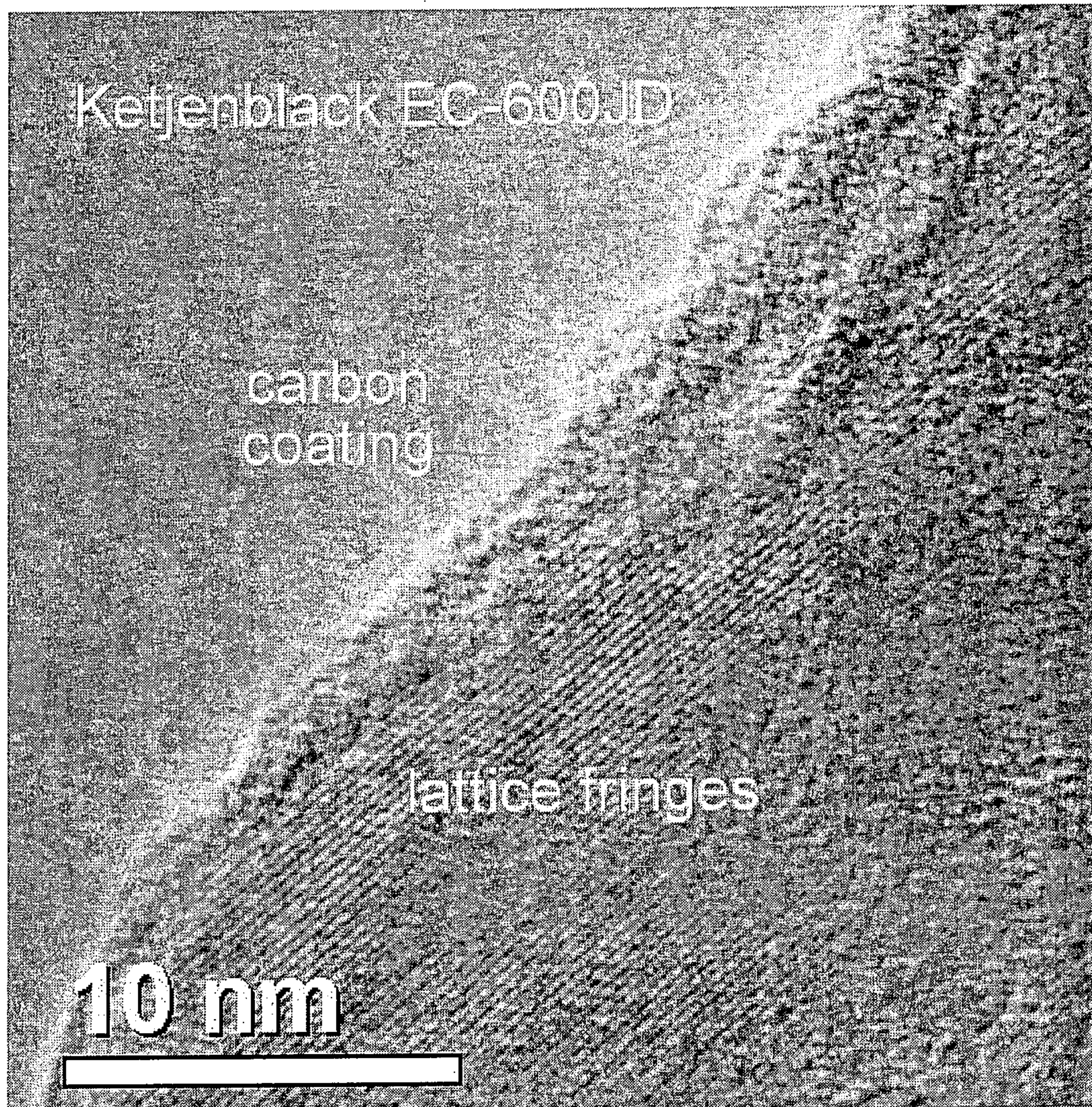


Figure 23

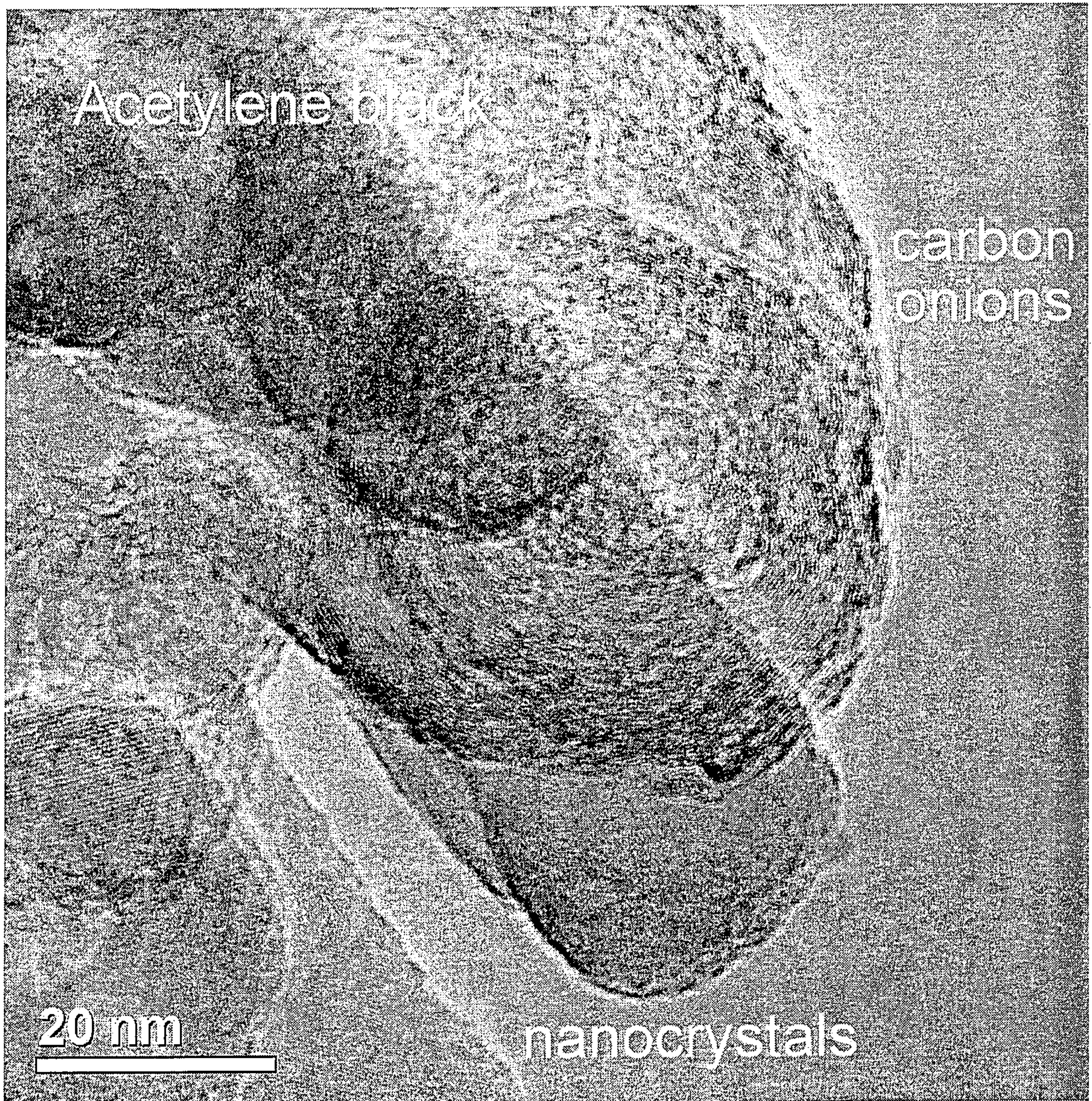


Figure 24

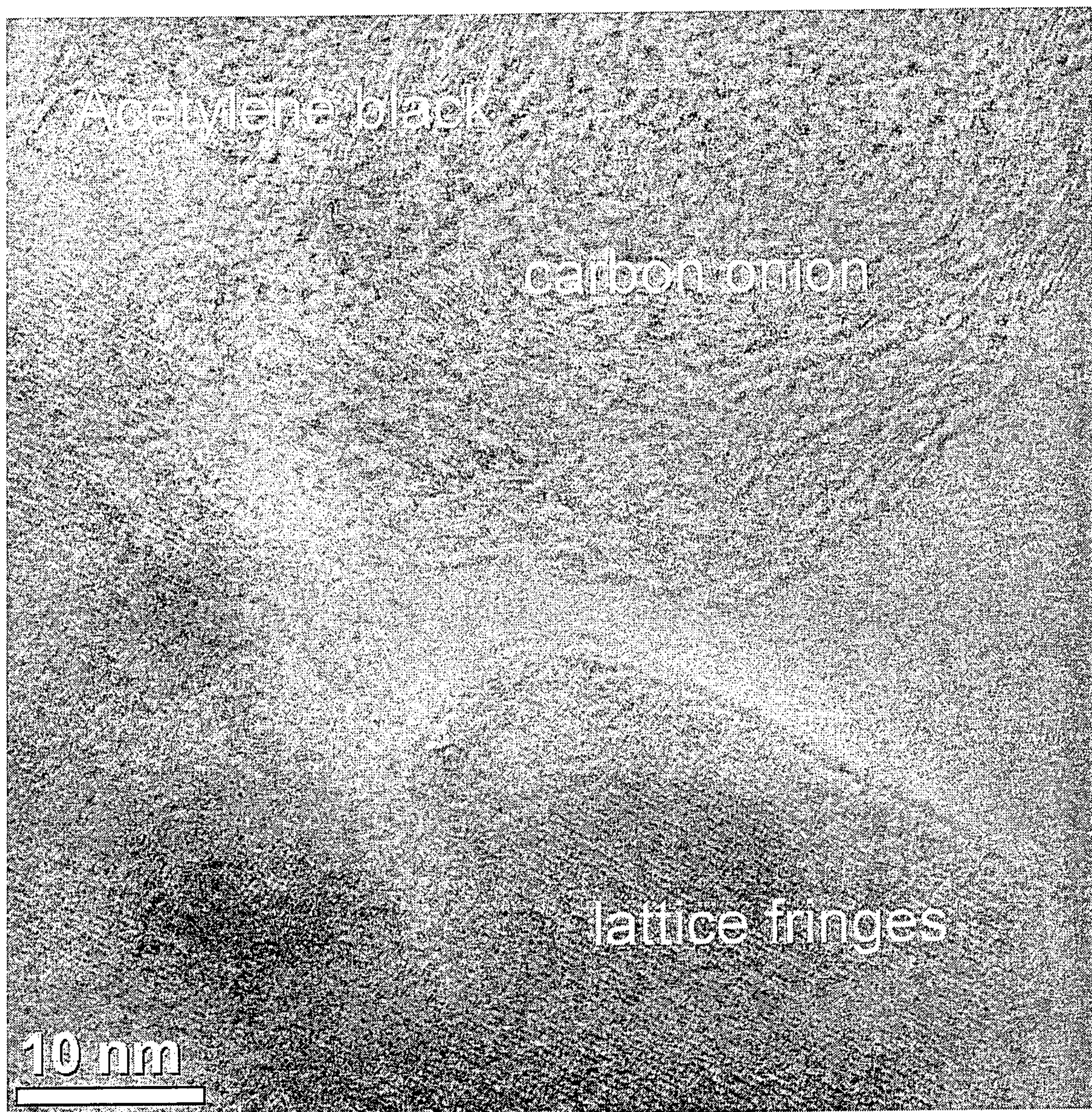


Figure 25

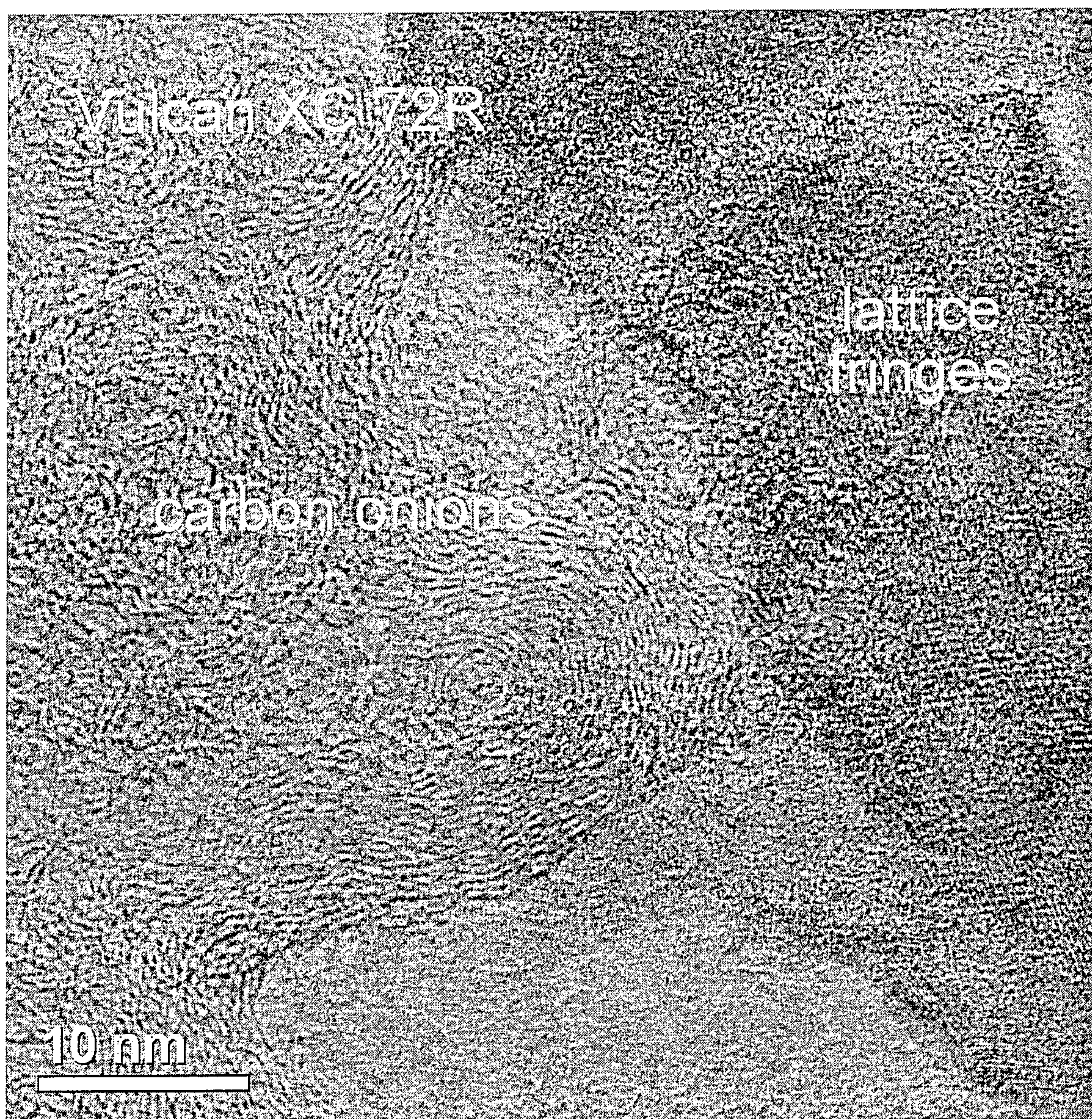


Figure 26

