



Short communication

2LiH + M (M = Mg, Ti): New concept of negative electrode for rechargeable lithium-ion batteries

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ABSTRACT

$x\text{LiH} + \text{M}$ composites, where $\text{M} = \text{Mg}$ or Ti , are suggested as new candidates for negative electrode for Li-ion batteries. For this purpose, the $x\text{LiH} + \text{M}$ electrode is prepared using the mechanochemical reaction: $\text{MH}_x + x\text{Li} \rightarrow x\text{LiH} + \text{M}$ or by simply grinding a $x\text{LiH} + \text{M}$ mixture. The most promising electrochemical behaviour is obtained with the $(2\text{LiH} + \text{Mg})$ composite prepared via a mechanochemical reaction between MgH_2 and metallic Li leading to a very divided composite in which Mg crystallites of 20 nm size are embedded in a LiH matrix. Reversible capacities of 1064 mAh g^{-1} (three times as much as the one of graphite) and 600 mAh g^{-1} are reached for these phase mixtures after 1 and 28 h of grinding in vertical and planetary mill, respectively. The $(2\text{LiH} + \text{Ti})$ mixture prepared via the mechanochemical reaction between TiH_2 and Li exhibits a reversible capacity of 428 mAh g^{-1} . From X-ray diffraction measurements, the performances of the electrodes are attributed to the electrochemical conversion reaction: $\text{M} + x\text{LiH} \leftrightarrow \text{MH}_x + x\text{Li}^+ + xe^-$ ($\text{M} = \text{Mg}, \text{Ti}$) followed for $\text{M} = \text{Mg}$ by an alloying process where M reacts with lithium ions to form $\text{Mg}_{1-x}\text{Li}_x$ alloys.

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1. Introduction

To satisfy the future market demand in terms of energy density, in the last decade, an intensive research has been devoted to the search of alternative negative electrode materials such as oxides, carbon or alloys [1–3] to overcome the intrinsic performances of the current used graphite limited to one lithium per formula unity.

In this context, we have recently demonstrated the reactivity of hydrides versus lithium ions through the conversion reaction: $\text{MH}_x + x\text{Li}^+ + xe^- \leftrightarrow \text{M} + x\text{LiH}$ ($\text{M} = \text{metal, alloy}$) [5]. As a promising consequence, metal hydrides [4] were suggested for the first time as a new family of negative electrodes for Li-ion batteries offering the advantage of coupling the high gravimetric and volumetric capacities of hydrides [5] with the required energy density of Li-ion batteries.

Going further in the understanding of the reactivity of this new class of materials, the electrochemical behaviour of $x\text{LiH} + \text{M}$ mixtures was investigated by preparing LiH/M composite using the mechanochemical synthesis of MH_x and Li powder or by directly grinding the LiH and M phases. Within this paper, the potential of $(x\text{LiH} + \text{M})$ mixture as new (candidate for) negative electrode material is discussed through two examples, namely $\text{M} = \text{Mg}$ or Ti .

2. Experimental

Commercial MgH_2 , TiH_2 and LiH powders were purchased from Aldrich. Li powder was provided by C.E.A.

Prior to being used in mechanical reaction and in order to increase their reactivity, MgH_2 (particle size: $40 \mu\text{m}$) and TiH_2 (particle size: $40 \mu\text{m}$) powders were initially ground 4 h in a vertical Spex 8000 mixer mill under argon in a 25 ml stainless-steel milling container with a ball to powder weight ratio of 10.

Mechanochemical reactions between MH_2 ($\text{M} = \text{Mg}, \text{Ti}$) and Li and the grinding of the $(2\text{LiH} + \text{M})$ mixtures were performed using two types of mixer mill: a vertical mixer mill, Spex 8000, and a planetary mill, Retsch PM100. The Spex mixer mill generates mainly impact/shock interactions as a result of the ball hitting the wall of the grinding container while the Retsch PM 100 (speed of 600 rpm) generates high shear interactions as the result of the ball rolling on the wall of the grinding container. In short, the Spex and the Retsch mixer mills mainly generate normal and tangential mechanical strain, respectively.

In order to avoid oxygen contamination, the preparation of the different mixtures, $(\text{MgH}_2 + 2\text{Li})$, $(\text{TiH}_2 + 2\text{Li})$, $(2\text{LiH} + \text{Mg})$ was realized inside an argon glove box. 1 gram of each mixture was placed with four stainless-steel balls of 10 mm in diameter, corresponding to a ball to powder ratio of 16, in a 50 ml stainless-steel container under argon atmosphere.

The X-ray diffraction measurements of the $(\text{MgH}_2 + 2\text{Li})$, $(\text{TiH}_2 + 2\text{Li})$, $(2\text{LiH} + \text{Mg})$ mixtures at different milling times and of the metal-hydride electrodes at various stages of the electrochemi-

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cal cycling were performed in a beryllium window sealed cell using a D8 BRUCKER diffractometer ($\lambda_{\text{Cu K}\alpha} = 1.54180 \text{ \AA}$) equipped with a Vantec detector.

The crystallite size L (nm) was measured from the full width at half height β of the X-ray diffraction patterns using the Scherrer formula: $L \text{ (nm)} = 0.94 \lambda / (\beta \cos \theta)$ where λ is the wavelength and θ the diffraction angle.

The electrochemical tests were performed in SWAGELOK cells assembled in an argon filled glove box, using as active material:

- The ($\text{MH}_2 + 2\text{Li}$, $M = \text{Mg, Ti}$) ground powder mixtures corresponding after milling time to ($y\text{LiH} + y/2\text{M}$) mixtures with $y < 2$ in the Retsch mixer mill and $y = 2$ in the Spex mixer mill. y is defined as the mole number of Li that has reacted with MH_2 .
- The ($2\text{LiH} + \text{M}$, $M = \text{Mg, Ti}$) mixture ground with the Retsch or the Spex mixer mill.

The powder mixtures (7–10 mg) were mixed with 20% of SP carbon (Black carbon from MM, Belgium) as positive electrode, lithium metal as negative electrode and a Whatman GF/D borosilicate glass fibre sheet saturated with a 1 M LiPF_6 electrolyte solution in 1:1 dimethyl carbonate (DMC)/ethylene carbonate as separator/electrolyte and cycled using a Macpile automatic cycling/data recording system (Biologic Co, Claix, France) operating in galvanostatic mode between 3 V and 0.005 V versus Li^+/Li . A cycling rate of one lithium in 10 h was used. In potential–composition curves, x corresponds to the number of moles of Li involved in the discharge/charge of the electrode.

To perform the X-ray diffraction patterns of the metal-hydride electrodes at various stages of the electrochemical cycling, the cells, once cycled to the required potential, were stopped and opened in a dry box. The electrode material was recovered and washed with DMC. The electrode material was then introduced in a beryllium window sealed cell for XRD analysis.

3. Results and discussion

3.1. $y\text{LiH} + y/2\text{Mg}$ obtained with the planetary mill

Fig. 1 represents the evolution of the X-ray diffraction pattern of the $\text{MgH}_2 + 2\text{Li}$ mixture as a function of the milling time in a planetary mill Retsch PM100. The starting mixture consists of lithium powder and tetragonal $\beta\text{-MgH}_2$ (SG: $P4_2/mnm$) with the presence of a small amount of orthorhombic metastable $\gamma\text{-MgH}_2$ (SG: $Pbcm$) phase resulting of ball milling. Upon milling, the X-ray diffraction patterns show a progressive disappearance of $\beta\text{-MgH}_2$ and the decrease in Li peaks intensities associated with the appearance of two well-defined sets of peaks located at $2\theta = 38.05^\circ, 44.30^\circ$ and $2\theta = 32.15^\circ, 34.30^\circ, 36.60^\circ$ corresponding to the main (1 1 1, 2 0 0) and (1 0 0, 0 0 2, 1 0 1) peaks of LiH (SG: $Fm3m$) and Mg (SG: $P6_3/mmc$). The latter reach their maximum intensity after 28 h of milling. This suggests that MgH_2 reacts with Li to form Mg and LiH via a mechanochemical reaction. Note that the main Bragg peak of Li (1 1 0) at $2\theta = 36.18^\circ$ is still present after 28 h of grinding indicating that the reaction is not complete.

The potential–composition profiles of the $y\text{LiH} + y/2\text{Mg}$ electrodes (Fig. 2a) recorded at different milling times show the existence of a small plateau located around 0.715 V followed by the increase in the voltage until the cut off at 3 V while a longer plateau located at 0.290 V is observed during the first discharge. The length of both plateaus increases with milling time.

The reversible capacity of the first cycle deduced from the difference between the charge and the discharge capacities (Fig. 2b) increases with the ball-milling time from 162 mAh g^{-1} ($t = 7 \text{ h}$) to

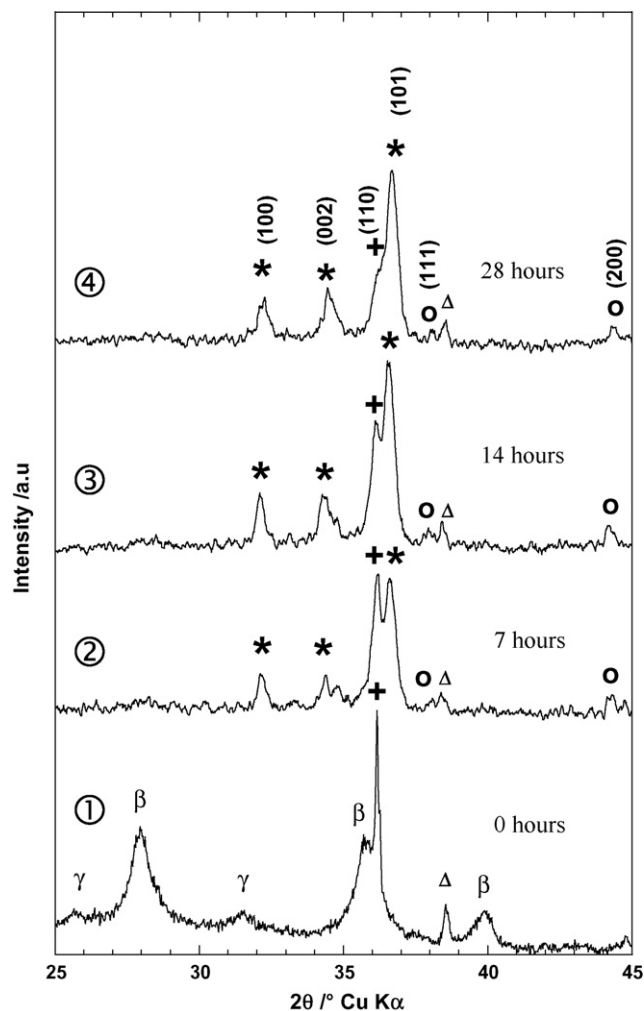


Fig. 1. Evolution of the X-ray diffraction patterns of the ($\text{MgH}_2 + 2\text{Li}$) mixture ground in the Retsch PM100 mixer mill as a function of milling time: (1) $t = 0 \text{ h}$, (2) $t = 7 \text{ h}$, (3) $t = 14 \text{ h}$, and (4) $t = 28 \text{ h}$. The X-ray peaks denoted *, β , γ , + and Δ correspond to Mg, $\beta\text{-MgH}_2$, $\gamma\text{-MgH}_2$, LiH, and Li respectively. Δ corresponds to the peaks of the X-ray cell.

610 mAh g^{-1} ($t = 28 \text{ h}$) while the irreversible loss decreases from 33% to 18%. The maximum capacity reached after 28 h of grinding (610 mAh g^{-1}) is far from the theoretical value (2038 mAh g^{-1}). This is not surprising as the mechanochemical reaction between MgH_2 and Li is incomplete.

3.2. $2\text{LiH} + \text{Mg}$ obtained with the vibratory mill

Aiming at evaluating the effect of different milling conditions on the formation of the ($2\text{LiH} + \text{Mg}$) phase mixture, the $\text{MgH}_2 + 2\text{Li}$ mixture was ball-milled in a vibratory mill Spex 8000. The XRD pattern obtained after 1 h of milling (Fig. 3) shows both the formation of metallic magnesium and lithium hydride associated with a total disappearance of the lithium and magnesium hydride phases suggesting a higher yield of reaction than that obtained with the planetary mill in agreement with more efficient impact interaction than shear interaction.

The electrochemical behaviour of the $2\text{LiH} + \text{Mg}$ composite prepared with the vibratory mixer mill is presented in the inset of Fig. 4. This curve has a similar shape (short plateau at 0.630 V in charge and a longer plateau at 0.388 V in discharge) than that previously recorded from the mixture synthesised with the planetary mill but shows higher charge and discharge capacities of 1.16 Li and 1.6 Li

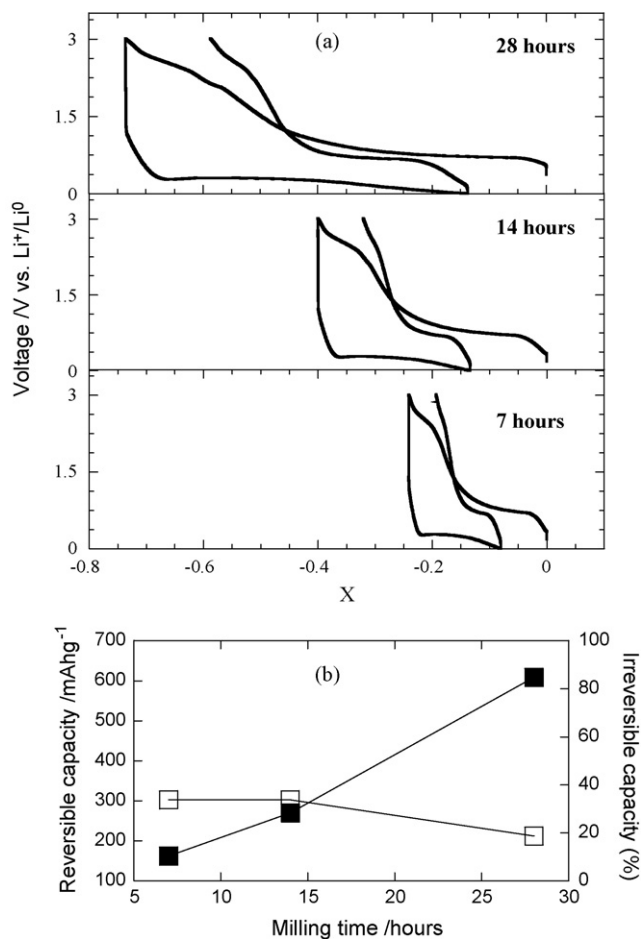


Fig. 2. (a) Potential–composition profile of the first cycle of the $(y\text{LiH} + y/2\text{Mg})/\text{Li}$ cell. (b) Evolution of the reversible (■) and irreversible (□) capacities of the $(y\text{LiH} + y/2\text{Mg})/\text{Li}$ cell with the milling time.

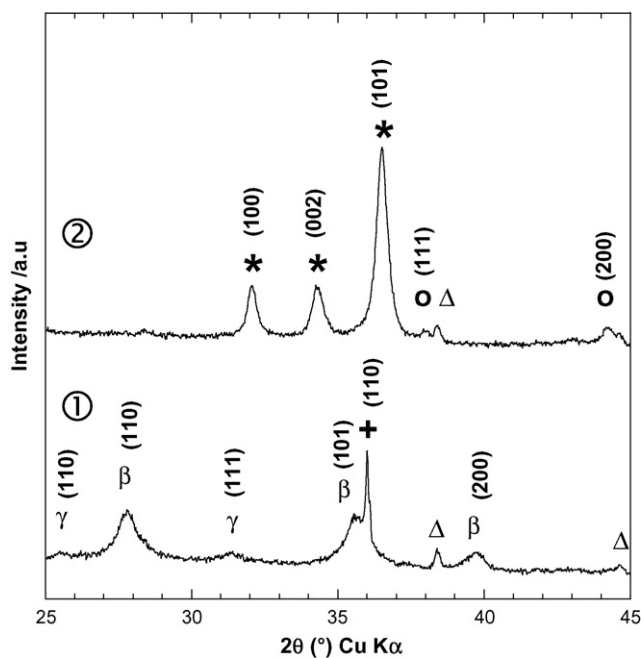


Fig. 3. X-ray diffraction patterns of the $(\text{MgH}_2 + 2\text{Li})$ mixture ground in the Spex 8000 mixer mill: (1) before ball-milling and (2) after 1 h of ball-milling.

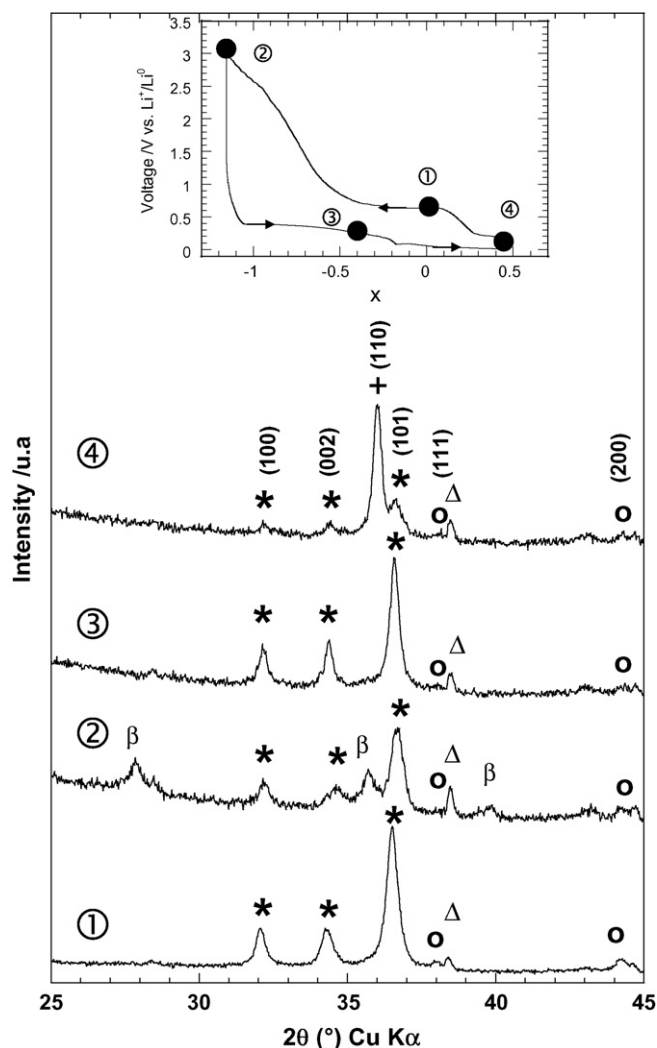


Fig. 4. X-ray diffraction patterns recorded at various stages of cycling of the $2\text{LiH} + \text{Mg}/\text{Li}$ cell: (1) starting material: $2\text{LiH} + \text{Mg}$ mixture ground in the Spex 8000 mixer mill: $x=0$, (2) end of the charge $x=-1.16$, (3) $x=-0.4$, (4) $x=0.45$. Inset: potential–composition profile of the first cycle of the $2\text{LiH} + \text{Mg}/\text{Li}$ cell. The X-ray peaks denoted $*$, β , γ and Δ in (1), (2), (3) correspond to Mg , $\beta\text{-MgH}_2$, $\gamma\text{-MgH}_2$ and LiH , respectively. In (4), the X-ray peaks denoted $*$ and $+$ correspond to Mg (hcp) and Li (bcc) solid solutions, respectively. Δ corresponds to the peaks of the X-ray cell.

compared to 0.8 Li and 0.5 Li for the mixture ground 28 h in the planetary mill (Fig. 2a), respectively.

In order to throw some light on the electrochemical mechanisms involved in the potential capacity curves of the $y\text{LiH} + y/2\text{Mg}$ mixture prepared with the vibratory and the planetary mill, the X-ray diffraction patterns have been recorded at the end of the first charge and during the first discharge. The X-ray diffraction pattern of the electrode collected at the end of the first charge (inset Fig. 4(2)) for the mixture obtained with the Spex mixer mill shows the appearance of MgH_2 hydride that coexists with unreacted Mg (Fig. 4(2)). When using the Retsch planetary mill, the formation of MgH_2 is also deduced from the X-ray diffraction pattern but with a lower MgH_2/Mg ratio (X-ray not shown here). It confirms the reaction of lithium hydride with magnesium to form magnesium hydride according to the theoretical reaction: $2\text{LiH} + \text{Mg} \rightarrow \text{MgH}_2 + 2\text{Li}^+ + 2\text{e}^-$

During the first cell discharge (inset Fig. 4), two plateaus were distinguished at 0.388 V (from $x=-1.16$ to $x=-0.4$) and 0.080 V (from $x=-0.2$ to $x=0.45$). The first one corresponds to the electrochemical conversion reaction of the *in situ* formed MgH_2 with

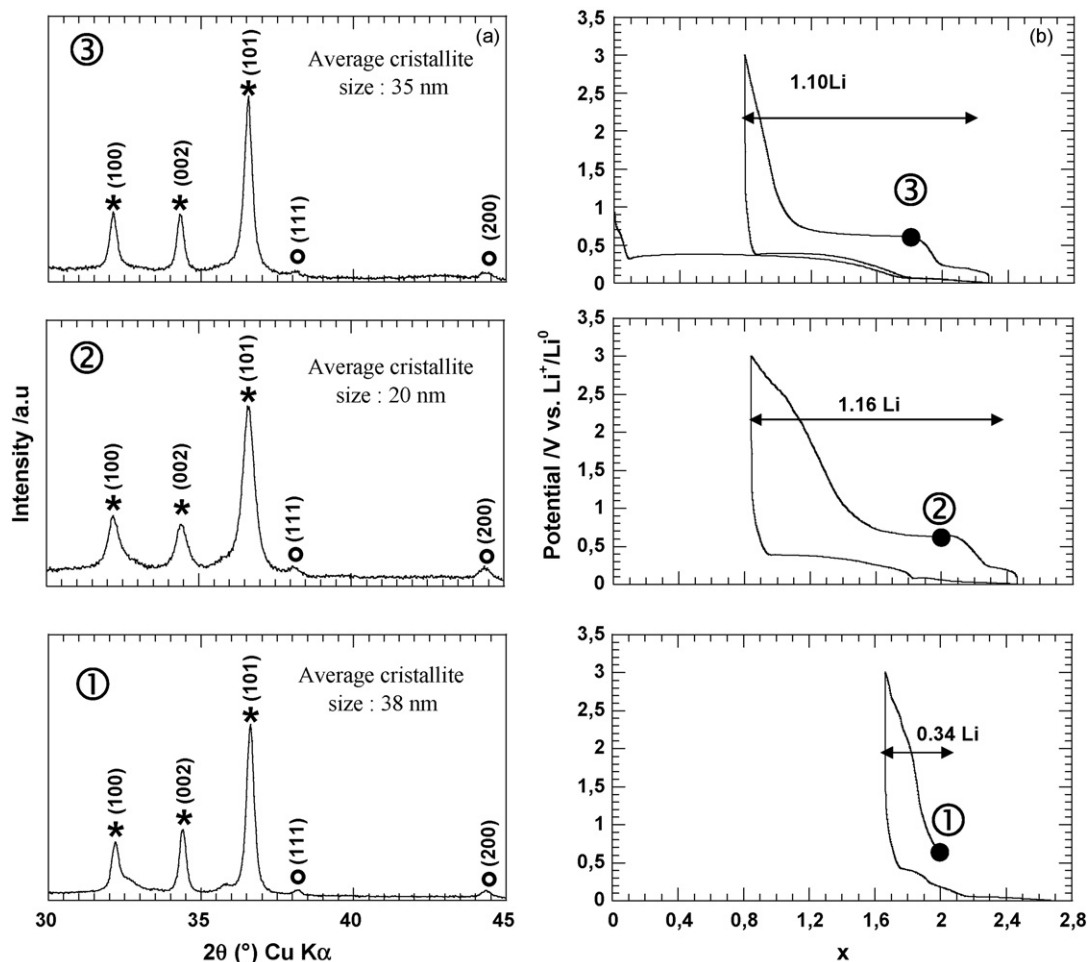


Fig. 5. (a) X-ray diffraction of (2LiH+Mg) mixtures produced by: (1) ball-milling of LiH with Mg in Spex 8000 mixer mill, (2) by mechanosynthesis of MgH₂+2Li, and (3) at the end of the MgH₂/Li cell discharge. (b) Potential–composition profile of: (1) (2LiH+Mg) mixtures produced by ball-milling of LiH with Mg in Spex 8000 mixer mill, (2) (2LiH+Mg) mixtures produced by mechanosynthesis of MgH₂+2Li, and (3) MgH₂/Li cell.

lithium ions to form Mg and LiH (Fig. 4(3)), the second plateau is attributed to the alloying reaction of Mg with Li leading to the equilibrium between hcp magnesium and bcc lithium solid solutions (Fig. 4(4)), both involving a total reversible capacity of 1064 mAh g⁻¹.

In order to emphasize the key role played by the LiH/Mg solid interface, the preparation of LiH+Mg composite was realized by simply grinding a (2LiH+Mg) powder mixture. The electrochemical behaviour of such (2LiH+Mg) electrode does not show any reactivity when the mixture is ground in the Retsch mixer mill while charge and discharge capacities, of 0.34 Li and 1 Li, are measured for the mixture ground with the Spex mixer milled (Fig. 5b (1)) respectively. In both cases, the smaller charge capacity of the 2LiH+Mg ground mixture than the one previously reported for the mechanochemical reaction (charge capacity $x=1.16$ Li) is due to the lack of reactivity between LiH and Mg related to a bad contact between Mg and hydrogen atoms of LiH and long distance between LiH and Mg particles.

When the composite is prepared via mechanosynthesis (Figs. 3a (2), 5a (2), and 5b (2)), the energy generates during the shock between the particles and the balls enables to trap the MgH₂ and the Li particles together and then to transform them via a solid state reaction in a (2LiH+Mg) mixture. In such powder, each particle is in a divided composite in which Mg with crystallite size of 20 nm is embedded in a LiH matrix. As a consequence, the increase of the number of Mg/LiH interfaces of this intimate phase mixture

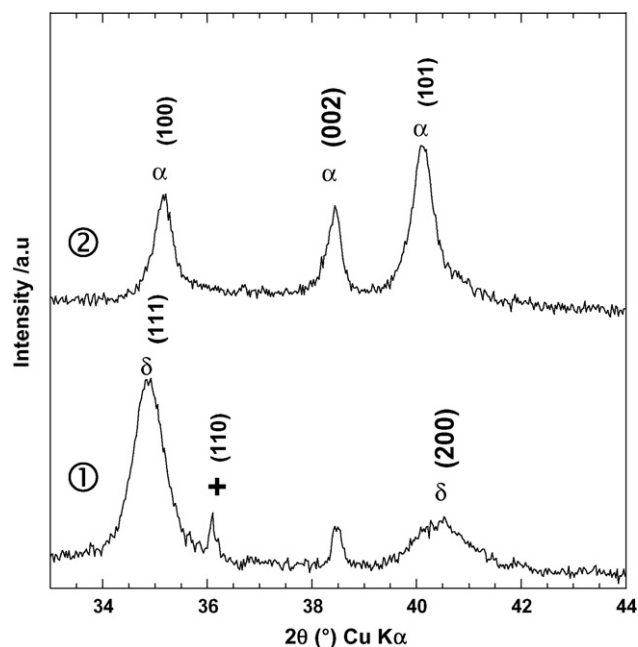


Fig. 6. X-ray diffraction patterns of TiH₂+2Li mixture with milling time: (1) starting mixture before ball-milling and (2) after 2 h of ball-milling in Spex 8000 mixer mill. The X-ray peaks denoted δ , α and + correspond to TiH₂, Ti and Li, respectively.

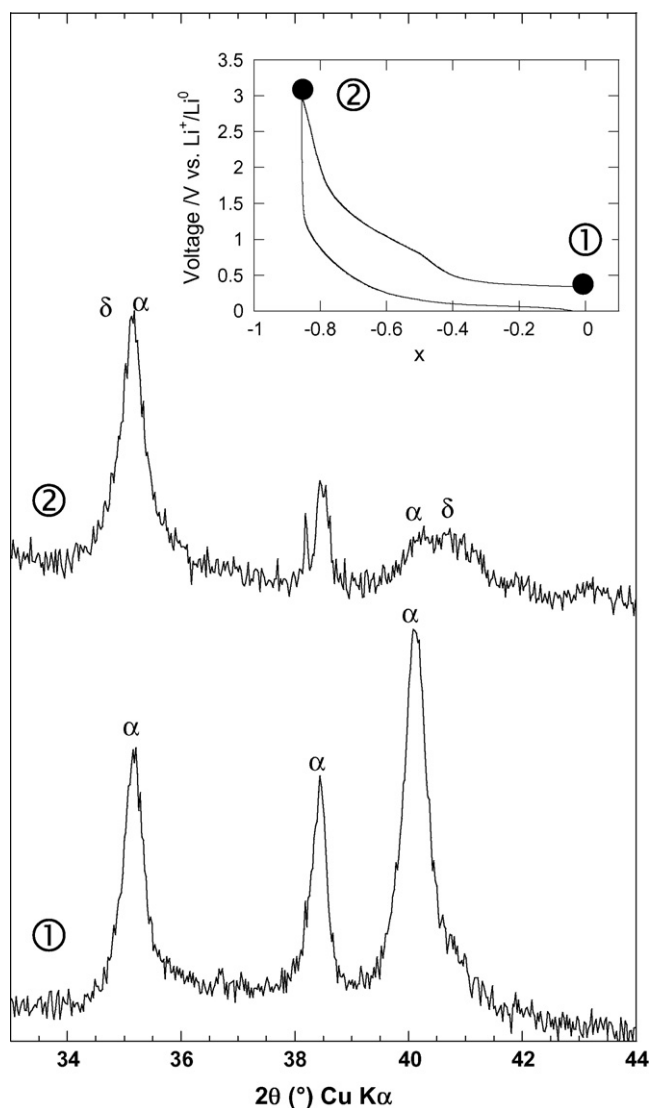


Fig. 7. X-ray diffraction patterns of: (1) $\text{TiH}_2 + 2\text{Li}$ after 2 h of ball-milling and (2) end of the $\text{Ti} + 2\text{LiH}/\text{Li}$ cell charge. The X-ray peaks denoted δ , α and $+$ correspond to TiH_2 , Ti and Li , respectively. Inset: potential–composition profile of the first cycle of the $2\text{LiH} + \text{Ti}/\text{Li}$ cell.

leads to the reduction of the H and Mg distances favouring the reformation of MgH_2 . So there is no doubt that the characteristics of the $(\text{Mg} + 2\text{LiH})$ composite used as prepared or formed during the first discharge will determine the future behaviour of the electrode. For instance, the comparison between the electrochemical profile of the $(2\text{LiH} + \text{Mg})$ electrode prepared via mechanosynthesis (Figs. 3a (2) and 5 (2)) and via electrochemical reaction from $\beta\text{-MgH}_2$ (Fig. 5b (3)) gives evidence of the role played by the particle size of the composite electrode obtained after discharge. In fact, a higher polarization and a lower reversible capacity is observed in the $(2\text{LiH} + \text{Mg})$ composite prepared by solid state reaction showing that the lithium extraction during the charge seems more difficult

than in the LiH and Mg mixture produced *in situ* during the electrochemical reaction $\text{MgH}_2 + 2\text{Li}^+ + 2\text{e}^- \rightarrow 2\text{LiH} + \text{Mg}$. This result is probably due to the higher density and the large strain remaining in the composite produced by mechanosynthesis. The agglomeration of the particles occurring during the grinding process plays an opposite effect on the lithium extraction compared to the one produced by the reduction of the crystallite size of the LiH/Mg composite. In contrast, in the electrochemical conversion process, a single particle of MgH_2 is involved in the formation of 2LiH and Mg phases and the volume expansion of 83% is only due to the lattice change between MgH_2 and $2\text{LiH} + \text{Mg}$.

It shows that if the formation of MgH_2 is dependent on the number of LiH/Mg interfaces, small particles size will help the lithium extraction by increasing the number of active material–liquid (i.e. electrolyte) interfaces.

3.3. $2\text{LiH} + \text{Ti}$ obtained with the vibratory mill

More interestingly, such reaction is not specific to Mg and can be extended to other metals. The second example presented in this paper concerns the $2\text{LiH} + \text{Ti}$ composite. A $2\text{LiH} + \text{Ti}$ mixture was prepared by a mechanical reaction of TiH_2 and Li . The $\text{TiH}_2 + 2\text{Li} \rightarrow 2\text{LiH} + \text{Ti}$ reaction was completed after 2 h of milling (Fig. 6 (2)) in a Spex apparatus.

The potential–composition profile (inset Fig. 7) shows a charge curve corresponding to the theoretical conversion reaction $2\text{LiH} + \text{Ti} \rightarrow \text{TiH}_2 + 2\text{Li}^+ + 2\text{e}^-$, as confirmed by X-ray diffraction pattern performed at the end of the first charge (Fig. 7 (2)), indicating the formation of titanium hydride. The capacity of the first charge is 455 mAh g^{-1} whereas after one cycle, the reversible capacity is 428 mAh g^{-1} indicating a capacity retention of 94%.

4. Conclusions

To summarize, the mechanochemical reaction of MH_x with Li powders performed in two types of mixer mill, leading to the formation of an $x\text{LiH} + \text{M}$ mixture where M is Mg or Ti , offers the possibility to use such composite as negative electrode material in lithium-ion batteries. The galvanostatic cycling reveals that for the $(y/2 \text{ M} + y\text{LiH})/\text{Li}$ cells the charge/discharge is a reversible process according to the theoretical conversion reaction: $\text{M} + x\text{LiH} \leftrightarrow \text{MH}_x + x\text{Li}^+ + x\text{e}^-$. Despite the improvement needed to optimize the yield of such electrochemical reaction as well as the electrode formulation in regards with the novelty of this concept, we believe that this new route to study the reactivity of hydrides with lithium ions will be helpful for the search of better negative electrode of general formula: $(\text{M} + x\text{LiH})$ or MH_x where M is a metal or an alloy.

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