MgH₂–CoO: a conversion-type composite electrode for LiBH₄-based all-solid-state lithium ion batteries†

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Several studies have demonstrated that MgH₂ is a promising conversion-type anode toward Li. A major obstacle is the reversible capacity during cycling. Electrochemical co-existence of a mixed metal hydride-oxide conversion type anode is demonstrated for lithium ion batteries using a solid-state electrolyte. 75MgH₂-25CoO anodes are obtained from optimized mixing conditions avoiding reactions occurring during high-energy ball-milling. Electrochemical tests are carried out to investigate the cycling capability and reversibility of the ongoing conversion reactions. The cycling led to formation of a single-plateau nanocomposite electrode with higher reversibility yield, lowered discharge-charge hysteresis and mitigated kinetic effect at high C-rate compared to MgH₂ anodes. It is believed that reduced diffusion pathways and less polarized electrodes are the origin of the improved properties. The designed composite-electrode shows good preservation and suitability with LiBH₄ solid electrolyte as revealed from electron microscopy analyses and X-ray photoelectron spectroscopy.

Introduction

Development of beyond-intercalation systems is of utmost importance for achieving novel Li-ion battery concepts.¹⁻³ Magnesium hydride has been demonstrated to be a candidate for conversion-type anodes,⁴⁻⁶ where the (de)lithiation processes are governed by a conversion mechanism, MgH₂ + 2Li ⇌ 2LiH + Mg. This material features a high theoretical capacity of 2037 mAh g⁻¹ toward lithium and low discharge-charge hysteresis.⁴ However, the reversible capacity is still limited owing to the poor conductivity of the involved entities (MgH₂/LiH), along with transient aging issues of LiH in carbonate-based liquid electrolytes.⁷⁻⁹ Using amorphous 80Li2S–20P2S5 as a solid electrolyte (SE), Ikeda et al.¹⁰ reported ~31% reversible capacity for MgH₂ for the 1st cycle at room temperature, compared to ~75% for liquid electrolytes.⁶ Possible interaction at the electrode/SE (80Li2S–20P2S5) interface is pointed out as a cause for the low reversible capacity.

When LiBH₄ is used as SE at 120 °C, better performance has been reported with high initial reversibility yield (~90%) in the presence of Nb₂O₅ catalyst,¹¹,¹² which decreases during cycling. Single phase LiBH₄ as SE, operating above its phase-transition temperature (Ttrans-ortho–hexa ≈ 113 °C) with the highly ion-conducting hexagonal phase, has been demonstrated for other electrode materials with many advantages;¹³⁻¹⁷ including flexible mechanical properties, strain-induced diffusion activation energy and formation of a stable composite with the MgH₂ anode.²²⁻⁻²⁵ Furthermore, it has been reported that LiBH₄-SE – in the presence of metal hydride anode – contributes to the enhancement of the mobility of Li⁺ ions by H⁻ exchange effects which seems to play a key role during the electrochemical cycling processes.¹¹,²⁶,²⁷ CoO negative electrode (~700 mA h g⁻¹) has been reported to undergo a conversion reaction similar to MgH₂, with formation of Co nanoparticles dispersed in the Li₂O matrix.²⁸ Its cycling performance is unrivalled to any other conversion-type anode over hundreds of cycles owing to privileged nanoparticles distribution with exalted reactivity.²⁹ However, the high working potential and large cycling hysteresis hinders its application in Li-ion batteries.²²,²₈ Pure CoO adopts a rock-salt type structure with the lattice parameter a = 4.258 Å. A few reports exist on oxide additions to MgH₂ anodes, but only in small amounts for catalytic purposes.¹⁰,¹¹,¹⁶,¹⁷ Accordingly, the present work aims the study of the effect of the addition of an electrochemically active oxide such as CoO (25 mol%) on the cycling performance of MgH₂ anode,
a mixture having a theoretical capacity around \( \sim 1350 \text{ mA h g}^{-1} \). The final goal is to promote the cycling reversibility and inhibit the formation of Li–Mg alloys for low voltage operation in the presence of an oxide with large voltage window and better cycling response upon discharge/charge. Considering the effect of the cell assembly (additives, heat treatment, mechanical pressing) which may influence the cycling performance,\(^{5,7,8,10,32}\) the optimization of the design of the battery cells was performed first with MgH\(_2\) electrode without CoO addition. The prepared and optimized composite electrodes were characterized using powder X-ray diffraction (PXD), X-ray photoelectron spectroscopy (XPS) and scanning transmission electron microscopy (STEM) before and after the electrochemical tests toward Li metal. The mechanistic and synergetic behaviours of the hydride–oxide paired anode are addressed for the first time in this contribution.

### Experimental

MgH\(_2\) (98% purity), CoO (99.9% purity) and Co (99.9% purity) were purchased from Alpha-Aesar. The MgH\(_2\) powders were ball-milled (24 h) under 50 bar H\(_2\) using a Fritsch Pulverisette 6 planetary ball-mill and dried in the glovebox using the Fritsch Pulverisette 6 planetary ball-mill with stainless steel vials and balls (ball-to-powder ratio \( 40 : 1\), rotation speed 400 rpm) to hydrogenate any metallic Mg impurities. The LiBH\(_4\) (95%) chemical was purchased from Sigma-Aldrich and stored in its delivery flask in an argon filled glove box. The LiBH\(_4\) was ball-milled for 3 h using the Fritsch Pulverisette 6 planetary ball-mill and dried overnight at 120 °C under dynamic vacuum. The carbon black Super P® (C\(_{SP}\), Timcal) was dried in the same way. Synchrotron radiation powder X-ray diffraction (SR-PXD) patterns were obtained at the Swiss-Norwegian Beamlines (SNBL, BM01), ESRF, Grenoble with a Pilatus 2M 2-dimensional detector and a wavelength of 0.78956 Å. The samples were contained in 0.5 mm borosilicate capillaries that were rotated \(90^\circ\) during 30 seconds exposure. The sample – detector distance was 345.97 mm. 1D data were obtained by integration of the 2D diffraction patterns using the program Bubble.\(^{33}\)

MgH\(_2\) and CoO were mixed using both an agate mortar/pestle and Spex mill. For battery tests, the MgH\(_2\)/CoO composite electrode and Li foil were used as active anode material and counter-reference electrode, respectively. The active material (MgH\(_2\) or MgH\(_2\)/CoO), C\(_{SP}\) and SE powders were weighed in a \(40 : 30 : 30\) mass ratio, and then hand mixed by an agate mortar/pestle to obtain a composite mixture. Around 50 mg of the SE was introduced first in a 15 mm die-set and pressed uniaxially at 100 MPa, and followed by 5 mg of the composite mixture and pressed together with Cu foil on top at 180 MPa. A Li foil was placed on the opposite side of the material composite. The resulted multi-layer pellet was inserted in a CR2032 coin cell fitted with PTFE gasket for cycling at 120 °C.

The following cells were assembled:

- **Battery cell (1):** MgH\(_2\)/C\(_{SP}\)/LiBH\(_4\) | LiBH\(_4\) | Li.
- **Battery cell (2):** MgH\(_2\)/CoO/C\(_{SP}\)/LiBH\(_4\) | LiBH\(_4\) | Li.

All sample handling was performed in a MBraun® glove box under argon atmosphere (H\(_2\)O and O\(_2\) < 1 ppm). The cells were cycled at different rates between 0.3–1 V, using a battery cycler (Hioki®, Japan). In this study, a voltage cut-off at 0.3 V was applied to avoid formation of Mg–Li solid solutions and thus focus on the main conversion reaction occurring around 0.5 V.\(^{46}\)

XPS technique was carried out using a Thermo Fisher Scientific ESCALAB 250Xi unit with an Al-K\(_\alpha\) (1486.6 eV) X-ray source. A dedicated sample holder was employed to transfer the powder samples from the glovebox to the vacuum chamber of the XPS without air exposure.

STEM was performed with a JEOL JEM-2100F microscope operated at 200 kV, with an Oxford 80 mm\(^2\) EDS detector. Focused ion beam-scanning electron microscopy (FIB-SEM) was carried out with a FEI Helios G4 dualBeam FIB. The Ga\(^+\) ion beam was used to cut down through the electrode for cross-section imaging, EDS analysis and STEM sample preparation. Owing to their high reactivity after cycling, the electrode samples for STEM/SEM were prepared with the addition of the polyvinylidene fluoride (PVDF) binder using the slurry method to protect the particles surface as short air exposure cannot be avoided.

### Results and discussion

Fig. 1 shows the SR-PXD patterns of the as-received CoO, mixed MgH\(_2\)/CoO before and after addition of the LiBH\(_4\) solid electrolyte and C\(_{SP}\) carbon black. The as-received CoO material is well crystalline without any impurity phases. After hand mixing of MgH\(_2\)/CoO, the corresponding pattern shows both tetragonal and orthorhombic MgH\(_2\) with major presence of the former modification in addition to CoO.

![Fig. 1](image-url)
Ball milling of MgH₂ and metallic Co is reported to result in formation of Mg₂CoH₅. We find that ball-milling MgH₂/CoO using Spex for 3 h is enough to form significant amounts of this phase. In this case, the analyzed patterns (Fig. S1 in ESI section†) indicate that MgH₂ is almost disappeared, while CoO still remains. During this solid-state reaction, the formation of water molecules may occur (hydrated or gaseous phase) which is beyond the scope of the present study. As the electrochemical performance of Mg₂CoH₅ compound is poor, its formation during the milling should be avoided. Thus, the preparation was then limited to hand mixing and Spex-milling with LiBH₄/CoO/CSP for 1 h, which ensure good dispersion without formation of Mg₂CoH₅ according to SR-PXD. TEM analysis indicates that the 24 h milled MgH₂ powders have an average particle size of about 150 nm. The starting hand-mixed CoO powders are in the micron range. However, after Spex-milling, Fig. S2 (ESI section†) shows well-dispersed CoO particles with sizes of 20–100 nm in the MgH₂/C matrix.

Preliminary battery tests were carried out with the MgH₂ single anode without CoO. Fig. 2a shows the notable reversible cyclability of the MgH₂-based anode with flat discharge/charge plateaus, mirroring merely the solid-state diffusion process. This behaviour agrees with the fact that the conversion reaction undergoes a stable separation in the three-phase system (MgH₂–LiH–Li) during the thermodynamic non-equilibrium state at constant current. The presence of solid solution reactions and how the different phases are formed at the early stage (nucleation/growth) of the conversion mechanism can be a subject of debate which are not approached in this study.

Furthermore, the cycling curves show no unwanted effects at extreme compositions. The sudden change in the slope after the charge-transfer process during lithiation may be explained by the poor conductivity of the native LiH formed at the MgH₂ surface. The resulting discharge/charge hysteresis is around 42 mV with a working potential of ~0.5 V; values close to the obtained ones in liquid electrolyte. A small perturbation around 0.7 V can be discerned, and it needs to be clarified if it is related to any interaction with the electrolyte as reported at higher voltage. Further cycling (Fig. 2b) shows the enhanced capacity retention compared to previous studies during the first 20 cycles even though no catalyst is employed here. Afterwards up to 50 cycles, the MgH₂ anode follows a progressive decrease of the capacity. Remarkably, owing to the high coulombic efficiency, the loss of the capacity may occur during discharge as observed in previous studies. Fig. 2c shows the variation of the capacity as function of the C-rate and cycle number for the MgH₂ battery cell. From C/20 to C/10, the capacity retention is unaffected by the C-rate during discharge and charge. At the highest employed C-rate (C/2), a kinetic effect can be observed and the capacity is somewhat lower than at C/10 and C/20 rates, but it does not decrease further over 5 cycles. It can be noticed that the kinetic rate seems to have more significant effect on the charge (LiH/Mg → MgH₂) than the discharge reaction (MgH₂ → LiH/Mg).

After assessing the performance of the MgH₂ anode, the electrochemical behaviour of the MgH₂–CoO composite electrode assembled in the same way as for the single anode needs to be elucidated. Fig. 3 shows the obtained discharge–charge galvanostatic profiles of the 75MgH₂–25CoO anode in which two reversible processes at 0.89 V and 0.5 V (inset of Fig. 3) can be distinguished during the first cycle. At discharge, the observed two plateaus are related to the successive reduction of CoO and MgH₂, respectively. It presents flat discharge–charge plateaus and low polarization-hysteresis; a remarkable electrochemical asset with high conversion yield. Higher capacity is observed for the first discharge which can be attributed to an activation process of the electrolyte/electrode interface as reported previously. Further cycling leads to the gradual decline of the 1st plateau in both discharge and charge, and its disappearance after 5 cycles.

This point needs to be clarified if the nanocrystalline nature of CoO/Co can be connected to the decline of the plateau and resulting to a pseudocapacitor behaviour. Interestingly despite the observed structural changes during the (de)lithiation
processes, the capacity retention remains less affected. During the first 5 cycles, about 94% of the capacity is retained compared to only 90% for MgH₂ anode. Such improvement could raise the question if the CoO/Co particles are incorporated in the MgH₂ matrix leading to a nano-composite with high reversibility yield and thus overcoming the issues of the electronic conductivity and particles aggregation. According to literature, CoO has been reported to undergo reversible cycling at constant current density with formation of nano-sized particles in the range of 1–2 nm. Such an eventual nanoscale interaction can make the Li ions and electrons available in close vicinity at the surface of MgH₂/Mg via the highly dispersive CoO/Co nanoparticles. At first glance, the interaction of Li₂O with Mg and LiH is not conceivable. These findings may suggest preferred reaction pathways for the composite-electrode system in a synergetic-like behaviour, and with a compromise between reversibility and kinetically-induced hysteresis offset by CoO and MgH₂ at different degrees.

Fig. 4a displays the rate capability of the MgH₂/CoO anode with good capacity retention and a coulombic efficiency close to 100%, except the 1st cycle after the rate is changed. Only slight decrease of the capacity can be detected at high rate (C/2). Contrary to MgH₂, in the MgH₂/CoO anode both discharge and charge states are sensitive to the C-rate. However, the composite-electrode exhibits a stable capacity and a good rate capability. *A priori* it seems like there is a beneficial kinetic effect from the presence of CoO. Fig. 4b shows the good cyclability of the MgH₂/CoO composite-electrode at high rate (C/2) with a moderate charge/discharge hysteresis of 75 mV compared to 32 mV obtained at C/20. This latter value is even lower than the one found for the MgH₂ anode (42 mV) at the same rate. At this stage it is difficult to conclude if this is related to mass effect or due to the presence of CoO, though the same total active masses (~2 mg) were used. However, the presence of CoO is clearly contributing to the improvement of the cyclability and reversibility while remaining active and delivering an extra capacity. Reduced diffusion pathways and less polarized electrodes are believed to be at the origin of such beneficial properties.

Fig. 5 shows the STEM observations of the electrode composite before cycling. The prepared sample section (Fig. 5a) reveals a homogenous electrode with the presence of small micro-cracks. EDS mapping (Fig. 5b and c) shows the Mg-based matrix with uniform distribution of CoO particles and with some C-rich areas. The CoO particles have an average size of about 50–100 nm in the uncycled electrode, in agreement with the first TEM analysis (Fig. S2†) of the as-prepared composite powders. The presence of O throughout
the sample comes from the inevitable short exposure to air between FIB preparation and STEM analysis.

A SEM-EDS map of the cross section of the interface between the electrode and the SE after 2 cycles is shown in Fig. 6. The electrolyte side can be distinguished by the B-rich region. The electrode part shows an even distribution of Mg and Co expected in the nano-range of few nm. According to cycling curves, MgH₂ is formed with possible presence of residual metallic Mg. Small amounts of O can be seen on the SE side, which may be due to possible surface contamination. Furthermore, O is depleted around Co (also seen in other maps), implying that some Co particles are metallic.

PXD analysis of the cycled electrodes yielded limited information, and the data were dominated by Bragg peaks from the electrode part shows an even distribution of Mg and Co expected in the nano-range of few nm. According to cycling curves, MgH₂ is formed with possible presence of residual metallic Mg. Small amounts of O can be seen on the SE side, which may be due to possible surface contamination. Furthermore, O is depleted around Co (also seen in other maps), implying that some Co particles are metallic.

The sample comes from the inevitable short exposure to air between FIB preparation and STEM analysis.

Fig. 6 Electron micrographs (FIB-SEM) of 75MgH₂-25CoO-based cell after 2 cycles at the electrode/electrolyte interface and the corresponding EDS mapping of the selected area.

Conclusions

New insights are reported for the enhancement of the reversible capacity of nano-composite electrodes combining two different materials with complementary electrochemical properties. A novel strategy is followed to improve the cycling performance of MgH₂ by adding an electrochemically active oxide, CoO. Battery
tests demonstrate possible co-existence of both MgH2/CoO anodes in a synergetic way, compensating mutually each other mainly regarding the mediocre reversibility of MgH2 and presence of highly dispersive CoO/Co nanoparticles. After prolonged cycling, the CoO plateau declines gradually, presumably owing to the nanocrystallinity of the involved entities in agreement with FIB-SEM analysis and XPS characterizations. The reversibility of MgH2 is confirmed by XPS while the CoO/Co entities are probably partially involved after cycling which may require the adjustment of the voltage window. Such electrochemical incorporation of CoO/Co nanoparticles in the MgH2 matrix is believed to contribute to the improvement of the cycling performance at high rates. This work may open up for a new composite-electrode concept where the electrochemical properties can be tuned for better cycling performance of electrode materials for application in all-solid-state batteries which will undoubtedly become a hot topic.

Conflicts of interest

There are no conflicts to declare.

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References


