Mg-based materials as anode for Li ion cells

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Metal hydrides demonstrated to be suitable materials for energy storage applications. Being hydrogen sorption reaction reversible for many hydrides they have been largely studied for hydrogen storage. In the case of batteries they can be used for the preparation of the electrolyte and of the electrodes, being an interesting alternative to compounds based on intercalation. In the case of the use of metal hydride in lithium ion cells, a conversion reaction takes place: $MH_x + xLi^+ + xe^- \leftrightarrow M + xLiH$*, where M is the metal. Being the reaction with* Li^+*, in suitable conditions, reversible, metal hydrides can be used to prepare anodes. Among different hydrides* MgH_2 *is particularly interesting as anode material presenting a large specific capacity (theoretical gravimetric capacity equal to 2038 mA/g) and low voltage hysteresis (about 300 mV) [1]. The conversion reaction take place at an average potential of 0.5 V versus* Li^+/Li*. Moreover* MgH_2 *is an environmental friendly and not a critical material.*

In this work MgH_2 *has been firstly activated by ball milling in stainless steel jars in a Spex 8000 mixer mill, also in presence of other compounds (Fe and* Nb_2O_5*). Successively anodes for Li ion cells have been prepared, in the form of discs, by mixing the powder with 20-30wt% of carbon nanostructures and PVDF. A coin cell has been assembled using the anode, prepared as described, a fiberglass Whatman separator impregnated with* $LiPF_6$*, as electrolyte, and a Li metal disc. The materials have been characterized by Scanning Electron Microscopy (SEM), X-Ray Diffraction, Surface area (BET), Thermogravimetric analysis (TG-DTA). Electrochemical measurements have been performed with a Maccor 4000, in the range 0.005-3.000 V. During the charge and discharge a current density of 0.1 C has been used. In some cases the characterization of the electrodes has been carried out before and after cell cycling to investigate the different phase formation.*

Convertion reaction
No intercalation reactions.
Formation of different compounds.
Redox reaction with Li^+ and formation of reduced M and LiX

$$M_xX_y + ne^- + nLi^+ \rightleftarrows xM^0 + yLi_mX$$

(m = n/y) (M = metal; X = F,P,O,H)

MgH_2

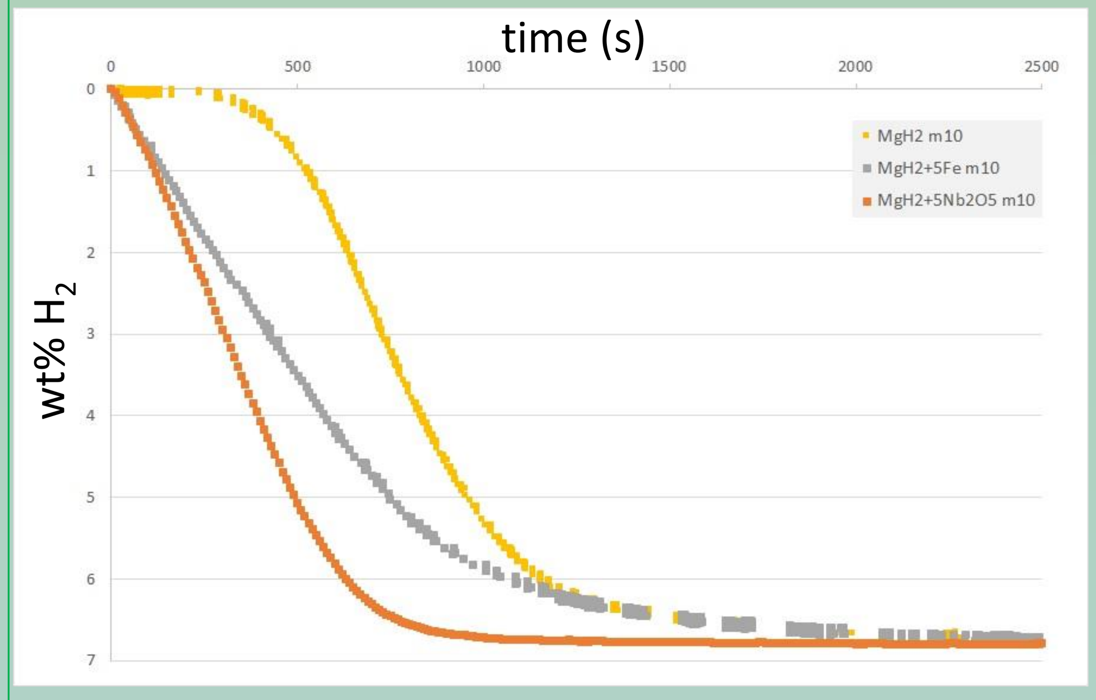
Volumetric capacity mAh/l	Gravimetric capacity mAh/g
2878	2038

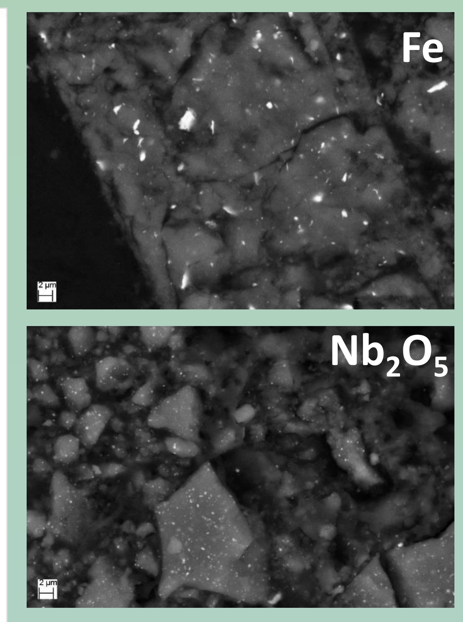
with working potential of 0.56 V vs Li^+/Li (Nerst equation)

Other Mg compounds

Compound	Gravimetric capacity mAh/g
Mg_2NiH_4	963
$MgFeH_6$	1456

MgH_2 as hydrogen storage material [2,3]

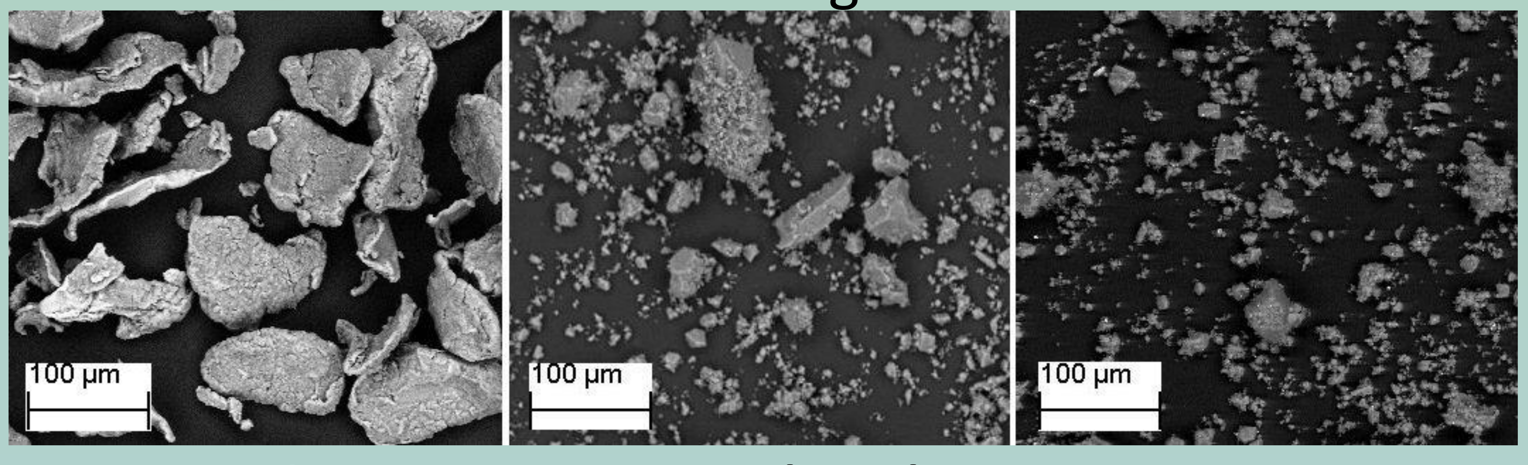




Kinetics of hydrogen desorption in samples MgH_2, MgH_2+5Fe and $MgH_2+5Nb_2O_5$ prepared by ball milling

Ball milling:
- Material activation;
- Particle refinement (nm);
- Alloying;
- Catalyst dispersion.

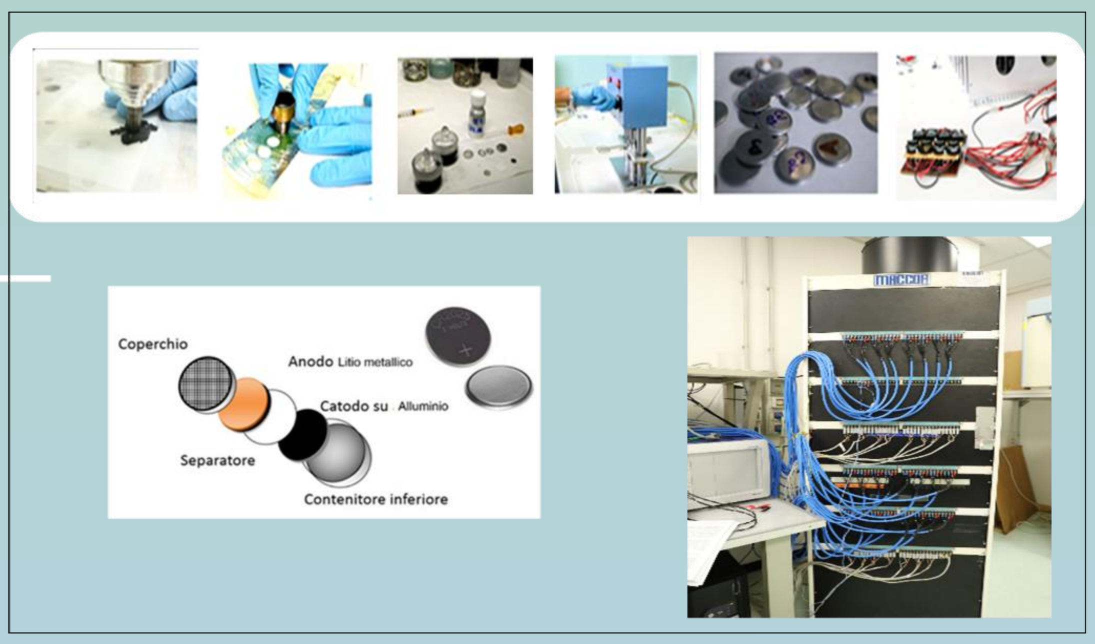
MgH_2 as — MgH_2 after ball milling — MgH_2 after cycling under hydrogen



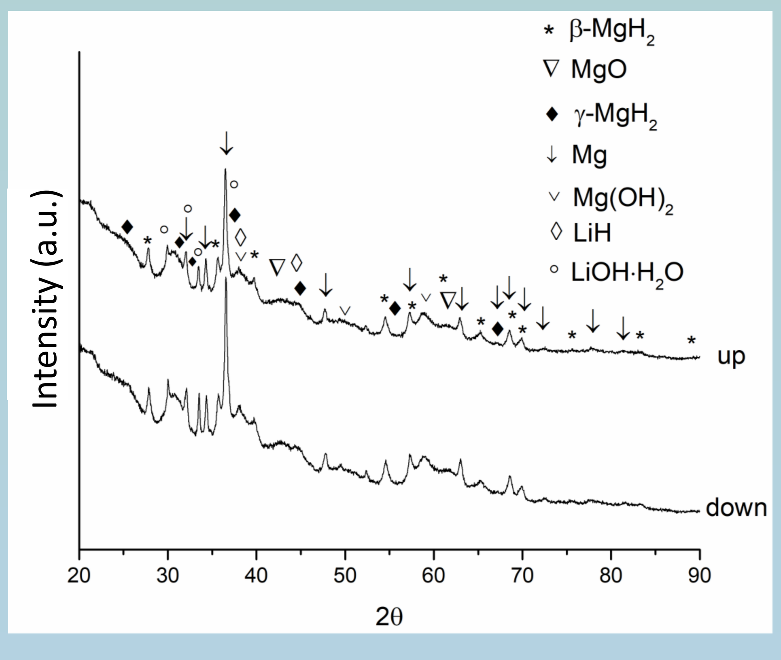
Scanning Electron Microscopy (SEM)

Surface Area (BET)

Materiale	BET surface area (m²/g)	Single point surface area at p/p°=.... : m²/g)	t-Plot Micropore Area (m²/g)	t-Plot External Surface Area (m²/g)	BJH Adsorption cumulative surface area of pores (m²/g)	BJH Desorption cumulative surface area of pores (m²/g)
MgH_2 as	2.98	at p/p°=0.300048600 : 2.9319	0.5342	2.4464	2.347	2.9993
MgH_2 BM m10	4.38	at p/p°=0.299995706 : 4.2996	0.4872	3.8922	4.526	4.8924
$MgH_2+5Nb_2O_5$ BM m10	4.49	at p/p°=0.301238853 : 4.4142	0.5813	3.9081	4.534	4.9248
MgH_2+5Fe BM m10	13.67	At p/p° =0.300282605 : 13.0109	-	15.8281	17.542	25.4257



Electrochemical measurements
- Anode: MgH_2+30%Super P+ 10% PTFE;
- Electrolyte: Whatman filters impregnated with $LiPF_6$;
- Cathode: Li foil



X-Ray diffaction (XRD)
- Performed after galvanostatic cycles;
- Presence of MgH_2 and Mg;
- Reversible but slow reaction;
- Potential presence of insulating LiH which hinders charge tranport;
- Potential presense of irreversible compounds due to contamination and cycling

Samples	Potential Range (Volt)	Capacity at first cycle ($mAhg^{-1}$)	Number of cycles	Plateau (Volt)	Weight of active material (mg)
MgH_2_mill_C	0,4-3	1300	46	0,3	4,3
MgH_2_Fe	0,4-1,4	1500	20	0,4	4,68
$MgH_2\_Nb_2O_5$	0,4-1,4	800	30	0.4	4,02
MgH_2_new	0,4-1,4	1400	30	0,4	4,2

Conclusions: metal hydrides are interesting materials for the preparation of anodes for Li-ion batteries, due to their high gravimetric and volumetric capacity and reversible reactions. In this work, ball milled MgH_2 was used as anode material. Electrochemical measurements showed a high capacity at first cycle which faded rapidly with cycling. Further research is required in order to develop strategies for reducing the capacity loss.

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