Electrochemical performances of MgH₂ and MgH₂-C films for lithium ion battery anode

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Abstract

As a high-capacity hydrogen storage material, MgH₂ also shows specific advantages for LIB anode. In this work, MgH₂ and MgH₂-C films were prepared by magnetron sputtering and hydrogenation treatment, and their microstructural and electrochemical properties were investigated. Through the conversion reaction of MgH₂ with lithium ($\text{MgH}_2 + 2\text{Li}^+ \rightarrow \text{Mg} + 2\text{LiH}$), the reversible lithium storage was achieved in the MgH₂ and MgH₂-C films. The MgH₂ film delivers the initial discharge capacity of 313.9 $\mu\text{Ah cm}^{-2}$ (~2956 mAh g⁻¹), the discharge and charge capacities related to the conversion process are respectively 150.0 $\mu\text{Ah cm}^{-2}$ (~1412 mAh g⁻¹) and 55.0 $\mu\text{Ah cm}^{-2}$ (~518 mAh/g), with the inefficiency of 63.3%. The GITT measurement determined the equilibrium potential of this conversion reaction to be 0.55 V vs. Li/Li⁺, and the voltage hysteresis between discharge and charge is only 10 mV vs. Li/Li⁺. In comparison with the MgH₂ film, the MgH₂-C film has smaller crystallite size, lower polarization effect and structural stability, but exhibiting lower capacity and equally poor cyclic performance. The poor cycle life of MgH₂-C film electrode is due to the large

irreversibility of conversion reaction of MgH_2 , instead of structural damage of film electrode during cycling.

Keywords: Lithium ion battery; Anode materials; MgH_2 ; Film; Magnetron sputtering; Electrochemical properties

1. Introduction

Despite the wide applications in the consumer electronics and electric vehicles for lithium-ion batteries (LIBs), high-capacity anode materials have always been the important research topic, aiming to meet the continuously increasing demand in the energy density [1, 2]. Compared with commercial graphite anode (372 mAh g^{-1}) with intercalation reaction mechanism, higher lithium storage capacity could be achieved in the metallic or semi-metallic elements (Al, Si, Ge, Sn, Sb, *etc.*) or in the M_aX_b -type compounds (M being a transition metal and X being F, O, P, N, S...) by alloying reaction or conversion reaction with lithium, respectively [3-5]. For example, the representative SnO_2 anode could deliver the conversion reaction capacity of 712 mAh g^{-1} ($\text{SnO}_2 + 4\text{Li} \rightarrow 2\text{Li}_2\text{O} + \text{Sn}$), and the alloying reaction capacity of 782 mAh g^{-1} ($\text{Sn} + 4.4\text{Li} \rightarrow \text{Li}_{4.4}\text{Sn}$) [6]. Over past decades, numerous conversion reaction anode materials have been investigated, through various nanostructuring and compositing strategies, great progresses have been achieved in improving the electrochemical performances in the irreversibility, cycling life, and rate capability [7-15].

Recently, metal hydrides were proposed as a new type of conversion reaction anode by Y. Oumellal *et al.* [16], the representative MgH_2 could deliver a reversible capacity of 1480 mAh g^{-1} (theoretical capacity 2038 mAh g^{-1}) by the conversion reaction: $\text{MgH}_2 + 2\text{Li}^+ \leftrightarrow \text{Mg} + 2\text{LiH}$. In addition, the MgH_2 showed much lower voltage hysteresis (below 300 mV) than other metal oxides, nitrides, sulfide, phosphides and fluorides [17]. Therefore, in addition to the existing application as the negative electrode of Ni-MH secondary battery, a large variety

of metal hydrides show application potential for LIBs anode [18-26]. However, like other conversion reactions anodes, pure MgH_2 electrode suffered large initial irreversible capacity loss and poor cycling performance, which was mainly attributed to the large volume variation (~85%) in the lithiation and delithiation process [16].

Several works indicate that the addition of carbon by ball-milling could effectively improve the discharge performances of MgH_2 , because of the enhanced conductivity and reduced crystallite size, which facilitates the diffusion of hydrogen and lithium [27-29]. By grinding of MgH_2 with a pre-ground carbon $\text{C}_{t,x}$ during 6 hours, Oumellal *et al.* [30] obtained a reversible capacity of 1480 mAh g^{-1} with an irreversible loss of 25%. By the bottom-up synthetic process from the organic precursor MgBu_2 , the Mg nanoparticles (~5.5 nm average size) was loaded into a carbon host, it showed enhanced cyclic stability with a capacity of $\sim 500 \text{ mAh g}^{-1}$ after 20 cycles [31]. However, the reversibility and cyclic stability of the MgH_2 composite electrode need to be further improved.

Generally, the ball-milled nanoscale MgH_2 has rather high reactivity with moisture, and thus the traditional slurry coating process in the air is not suitable for the preparation of MgH_2 electrode. For that, the researchers have to compact the powder mixture of MgH_2 , super P and binder into a disc or into a Ni foam in the Ar-filled glovebox, and the obtained MgH_2 powder electrode has low compact density and may cause the electrode failure during the cycling. Film electrode is an effective method to investigate the electrochemical performances and reaction mechanism of novel electrode materials because of convenient composition and microstructure control. Thin film growth techniques such as physical or chemical vapor deposition are also very well suited for micro-battery and thin film battery applications [32-35]. Further, the nanostructured films could be easily obtained under well controlled conditions, which could help to obtain good electrochemical activity and kinetics [36-38]. Therefore, the integrated binder-free film electrode with nanocrystalline structure is a possible route to enhance the cycleability of MgH_2 .

Herein this work, the MgH_2 film was prepared by magnetron sputtering and subsequent hydrogenation treatment, and the electrochemical properties of MgH_2 film electrode were investigated. In addition, to improve the conductivity of MgH_2 , we also prepared the Mg-C film from the Mg-C composite target, and the electrochemical properties were compared with pure MgH_2 film. The failure mechanism of the MgH_2 and MgH_2 -C film electrodes was also investigated.

2. Experimental

2.1. Film preparation

Mg and Mg-C films were firstly deposited on the Cu foil or Si wafer by radio frequency (RF) magnetron power (Mantis deposition system QPREP500, UK) using the Mg target (99.99 purity) and Mg-C composite target, respectively. In the Mg-C composite target, four graphite plates are embedded in the Mg disk, as schematically shown in Fig. 1. Before the deposition of Mg film, a thin Nb layer was deposited to prevent the reaction between the Cu foil and the Mg film in the hydrogenation treatment. In addition, a thin Pd layer was coated on top surface of Mg and Mg-C films to protect Mg against oxidation as well as catalyze the hydrogenation of Mg. The sputtering parameters for the film deposition are given in Table 1. Afterwards, the obtained Mg and Mg-C films were placed in a stainless-steel vessel and hydrogenated under 4 MPa hydrogen pressure and 300 °C for 8 h.

2.2. Material characterization

The microstructure of as-deposited films was characterized by X-ray diffraction (XRD) on PANalytical Empyrean diffractometer with $\text{Cu K}\alpha$ -radiation, and scanning electron microscope (SEM, Zeiss Supra 40 FE-SEM). The XRD test of as-deposited and as-hydrogenated films was performed in a glazing mode with the incident angle of 3°. The composition of Mg-C film was analyzed by energy dispersive X-ray analysis (EDS) with a Bruker QUANTAX spectrometer. The film thickness was measured by a surface profiler (Bruker DektakXT), and the obtained thickness of films is also shown in Table 1.

2.3. Electrochemical measurement

The hydrogenated Mg and Mg-C films with the Cu foil substrate were cut into round pieces of 12 mm in diameter, and used as the working electrodes. The net weight of each round piece (the area of 1.13 cm^2) of MgH_2 or $\text{MgH}_2\text{-C}$ film is estimated to be $\sim 0.12 \text{ mg}$ and $\sim 0.10 \text{ mg}$, respectively, which is the average value by measuring the area ($\sim 34.87 \text{ cm}^2$) and mass ($\sim 300 \text{ mg}$) of a whole Cu foil. However, the actual weight for each piece of film electrode is not same. The Coin cells (CR 2016) were assembled in an Ar-filled glovebox, using Li metal foil as counter and reference electrodes. The electrolyte was 1M LiPF_6 (1 M)/EC: DEC (1:2 in volume) with 10% FEC. The galvanostatic charge/discharge tests were carried out using a battery measurement tester (Land CT2001A). To measure the equilibrium potential of MgH_2 film electrode, the GITT test was performed on Land battery tester with constant current density of $10 \mu\text{A cm}^{-2}$, the film electrode was discharged for 2 h, and then followed by 10 h of relaxation. The procedure was repeated for 10 times with the cutoff voltage 0.2 V. Same charging conditions were also used in the charge process, but with the cutoff voltage 2 V. CV and EIS measurements were performed on an electrochemical workstation (Gamry Interface 1000). The CV test was performed at a scan rate of 0.2 mV s^{-1} with the voltage range 0-2 V. For the EIS test, a sine wave was used with the amplitude of 5 mV ranging 0.01 Hz to 100 kHz at selected discharge voltages in different cycles.

Table 1 The sputtering parameters and thickness of films.

	Mg film	Mg-C film	Pd film
Targets	Mg	Mg-C	Pd
Deposition time	60 min	60 min	1 min
Deposition power	200 W	200 W	100 W
Thickness	$\sim 220 \text{ nm}$	$\sim 270 \text{ nm}$	$\sim 6 \text{ nm}$
Base pressure	$4 \times 10^{-5} \text{ Pa}$		
Working pressure	0.4 Pa		
Substrate temperature	Room temperature		
Gas used	Ar (99.999%)		

3. Results and discussion

3.1 Microstructure of films

Fig. 2 shows the XRD patterns of as-deposited and hydrogenated Mg and Mg-C films with Si wafer. The strong Mg (002) diffraction around 34.3° indicates the preferential growth of Mg film (Fig. 2a). The broad peak around 40.4° is attributed to thin Pd layer. In the hydrogenated Mg film (Fig. 2b), the diffractions at 27.9° , 35.8° , 39.9° and 54.6° are assigned to tetragonal α -MgH₂ phase. Meanwhile, the residual Mg (101) and (110) diffractions around 36.8° , 57.5° are also observed in Fig. 2b, indicating the incomplete hydrogenation of Mg film. This is due to sluggish hydrogen diffusion in the MgH₂ lattice. Comparing with Mg film at as-deposited and hydrogenated states, the Mg-C film shows no distinct difference in the phase structure, and no any diffractions of graphite or Mg-C compound are present in Fig. 2c. Fig. 2d shows that the Mg is completely hydrogenated into MgH₂. Therefore, the hydrogenated Mg film and Mg-C film are denoted as MgH₂ film and MgH₂-C film, respectively.

Fig. 3 shows the SEM surface morphologies of as-deposited and hydrogenated Mg film and Mg-C film with the Cu foil substrate. A typical island-like microstructure is formed in the Mg film and Mg-C film (Fig. 3a), and the micro-sized islands ($<5\ \mu\text{m}$) consist of hexagonal Mg crystallites with the grain size of $\sim 160\ \text{nm}$. In addition, there exist widespread ravines among Mg particles for both Mg and Mg-C film. The rough surface morphologies of Mg film and Mg-C film is rarely reported in the previous work using the polished Si wafer [39-41], and it should be related to the Cu foil substrate with large surface roughness. In the MgH₂ film (Fig. 3b) and MgH₂-C films (Fig. 3d), the hexagonal edges of Mg crystals become blurred, which is due to the volume expansion with the phase transition of $\text{Mg} \rightarrow \text{MgH}_2$. In addition, the EDS analysis indicates that the average composition of Mg-C film is 68.2%Mg–31.8%C at molar ratio, and the element mapping results (Fig. 3e) demonstrates the homogeneous distribution of carbon in the Mg-C film.

3.2 Electrochemical performance of MgH₂ and MgH₂-C film

Fig. 4a shows the initial discharge and charge curves for the MgH₂ film in the voltage range 0.01-2.0 V. In the first discharge process, the potential drops down to 0.1 V, and then gradually increases up to ~0.36 V, which should correspond to the conversion reaction of MgH₂ with lithium. The observed over-potential is due to the poor conductivity of MgH₂ film, and the conversion reaction mechanism that involves a nucleation step. Afterwards, a short plateau occurs at 0.2 V, and the subsequent discharge at much low potential is related to the multi-step alloying of Mg with lithium. The MgH₂ film delivers the initial discharge capacity of 313.9 $\mu\text{Ah cm}^{-2}$ (~2956 mAh g⁻¹), of 150.0 $\mu\text{Ah cm}^{-2}$ (~1412 mAh g⁻¹) is related to the conversion reaction. In the charge process, the delithiation reaction below 0.15 V and the plateau at 0.6 V should be respectively attributed to the de-alloying of Mg(Li) and the reversible formation of MgH₂ from the Mg/LiH, contributing 55.0 $\mu\text{Ah cm}^{-2}$ (~518 mAh g⁻¹). The large initial discharge capacity indicates that the *in-situ* formed Mg has high electrochemical activity with lithium. So far, few studies were carried out on the electrochemical alloying reaction of Mg-Li system, because of high impedance film on the Mg surface. Park *et al.* [42] reported that the mechanically milled Mg-C composite showed an increased rate capability. In this work, the high electrochemical activity of Mg should be attributed to its small and clean MgH₂ crystallites.

The two-step reaction of MgH₂ film electrode is also confirmed by the cyclic CV curves as shown in Fig. 4b. With the scanning rate of 0.2 mV s⁻¹, the MgH₂ film electrode shows an obvious activation process, as indicated by increasing peak intensity with the cycle number. This result indicates the slow conversion reaction kinetics of MgH₂→Mg. In the 3rd cycle, it clearly shows the presence of two pairs of redox peaks: the reduction peak at ~0.17 V and the corresponding oxidation peak at ~0.7 V are attributed to the conversion reaction of Mg/MgH₂, the other pair at ~0.01 V and ~0.2 V is assigned to the de/-alloying of Mg with Li.

Fig. 4c shows the GITT curve of MgH_2 film electrode at the first discharge and charge cycle. The obtained average equilibrium discharge potential of 0.55 V vs. Li/Li^+ is much close to the theoretical value (0.56 V vs. Li/Li^+), which could be calculated by the Nernst law ($E = -\Delta_r G / 2F$, $\Delta_r G = -108.2 \text{ kJ mol}^{-1}$) [16, 43, 44]. As shown in the inset of Fig. 4c, the voltage hysteresis between the charge and discharge is determined to be only 10 mV, which is much lower than other conversion reaction anode materials.

Fig. 4d shows the cyclic discharge/charge voltage profiles of MgH_2 film electrode. To avoid the alloying of Mg with lithium at a low potential, the cutoff voltage in the cyclic test is set to be 0.2 V. In addition, due to the large polarization in the first discharge, a capacity limit (150 μAh) is also set as the ending condition for the first discharge. As shown in Fig. 4d, the MgH_2 film electrode shows a rapid capacity fading within 10 cycles. The initial discharge and charge capacities are 132.7 $\mu\text{Ah cm}^{-2}$ ($\sim 1249 \text{ mAh g}^{-1}$) and 38.8 $\mu\text{Ah cm}^{-2}$ ($\sim 365 \text{ mAh g}^{-1}$) respectively, with an irreversible capacity loss of 70.7%. This result implies that only part of MgH_2 could be reversibly formed from the Mg/LiH . In the 2nd cycle, the discharge potential increases up to 0.45 V from initial 0.34 V, and the discharge capacity decreases down to 50 $\mu\text{Ah cm}^{-2}$ ($\sim 470 \text{ mAh g}^{-1}$), which is even higher than the initial charge capacity. The additional discharge capacity should be attributed to the unreacted MgH_2 in the first cycle, while the voltage increase is due to the fact that the nucleation step is done and the presence of metallic Mg that could increase the electrode conductivity. Obviously, the reaction irreversibility of Mg/LiH is mainly responsible for the poor cyclic performance of MgH_2 film electrode.

Fig. 5a shows the initial discharge and charge curves of $\text{MgH}_2\text{-C}$ film electrode in the voltage range 0.01-2.0 V. Comparing with the MgH_2 film electrode, the $\text{MgH}_2\text{-C}$ film electrode displays much lower polarization effect, which is attributed to the enhanced conductivity by the carbon addition. The initial discharge and charge capacities are 126.5 $\mu\text{Ah cm}^{-2}$ ($\sim 1429 \text{ mAh g}^{-1}$) and 74.5 $\mu\text{Ah cm}^{-2}$ ($\sim 842 \text{ mAh g}^{-1}$) respectively, both of which are

lower than those for MgH_2 film. Similar two-step reaction characteristic is also found in the $\text{MgH}_2\text{-C}$ film, which is further verified by the CV curves (Fig. 5b). In the 2nd cycle, a pair of redox peaks occurring at 0.24 V and 0.68 V is assigned to the conversion reaction of MgH_2 with Li. The other pair of peaks is located at 0.01 V and 0.21 V, corresponding to the alloying of Li into Mg.

Fig. 5c shows the cyclic discharge/charge curves of $\text{MgH}_2\text{-C}$ film electrode, with the discharge cutoff voltage 0.2 V. In order to avoid the polarization in the first discharge, a capacity limit (80 μAh) is also set as the ending condition for the first discharge. The initial discharge and charge capacities are 70.8 $\mu\text{Ah cm}^{-2}$ ($\sim 800 \text{ mAh g}^{-1}$) and 33.6 $\mu\text{Ah cm}^{-2}$ ($\sim 380 \text{ mAh g}^{-1}$), respectively, and the initial Coulombic efficiency of $\text{MgH}_2\text{-C}$ film is 47.5%. Comparing with MgH_2 film, the $\text{MgH}_2\text{-C}$ film has lower initial discharge potential ($\sim 0.22 \text{ V}$), which should be due to the hindered Li^+ diffusion by the amorphous carbon. Similar with MgH_2 film electrode, the $\text{MgH}_2\text{-C}$ film electrode also shows fast capacity fading, the discharge capacity at 5th cycle is decreased down to 11.6 $\mu\text{Ah cm}^{-2}$, and the discharge potential is even lower than that at 2nd cycle.

Fig. 5d presents the Nyquist plots for the $\text{MgH}_2\text{-C}$ film electrode at the partially lithiated state with the cutoff voltage of 0.2 V in various cycles. For each Nyquist plot, there exist two greatly depressed semicircles in the high and medium frequency range, the first one corresponding to the impedance of surface film related to the electrolyte decomposition, and the second one corresponding to the impedance of the charge transfer occurring at the surface of the electrode. The inclined line in the low frequency range corresponds to the Warburg impedance which is related to the Li^+ diffusion in the bulk electrode. The inset of Fig. 5d clearly shows that the semi-circle among high-frequency well overlaps in each cycle, implying the stable resistance of surface film of electrode in different cycles, which should be contributed by the good structural integrity of the $\text{MgH}_2\text{-C}$ film. It is noted that the resistance

of the whole cell system is rather high, this should be due to the intrinsic low conductivity of MgH_2 (band gap at 5.6 eV) even by the carbon addition.

To investigate the failure mechanism of MgH_2 and $\text{MgH}_2\text{-C}$ film electrodes, the SEM images of MgH_2 and $\text{MgH}_2\text{-C}$ films after 10 discharge/charge cycles are shown in Fig. 6. In comparison with that at hydrogenated state (Fig. 3b), the film structure becomes loosing for both MgH_2 and $\text{MgH}_2\text{-C}$ films, which is due to the repeated volume expansion/shrinkage in the lithiation/delithiation process. However, the structural integrity of MgH_2 and $\text{MgH}_2\text{-C}$ films is remained. Further, the Mg crystallites still remains the hexagonal shape. Therefore, it is reasonably deduced that the poor cycling of MgH_2 and $\text{MgH}_2\text{-C}$ films should be due to the electrochemical deactivation on the surface of Mg crystals, which hinders the reverse reaction of Mg/LiH.

Regarding the low reversibility of conversion reaction of MgH_2 in Li-cells, it is possibly related to the specific performances of the metal hydrides MgH_2 and LiH. On the one hand, the delithiation product LiH has higher activity than MgH_2 . Unlike stable Li_2O for conversion reaction oxide materials, the LiH may become inactivated in the Li-cell environment. The passivated surface of LiH and the interface with Mg would not be beneficial to the reverse conversion reaction. On the other hand, the continuous formation of MgH_2 in the delithiation process requires the hydrogen diffusion through the MgH_2 lattice, which has been demonstrated to be very sluggish [45]. This is a possible kinetic reason for the low reversibility of conversion reaction of MgH_2 . To overcome these problems, building core-shell or yolk-shell nanoarchitecture may be an effective strategy, which has been shown to greatly improve the cyclic performances of high-capacity anode materials such as Si, Al, and Sn, *etc.* [46-52]. This is because of three specific advantages: 1) The shell could prevent the direct contact between active material and liquid electrolyte. Certainly, the shell could play as the electron and lithium conductor. 2) The shell could confine the pulverized active materials into a sealed space, avoiding the loss of active materials. 3) The nanosized MgH_2 core could

shorten the hydrogen diffusion distance. Therefore, a protective and active coating on the nanostructured MgH_2 film, such as the TiO_2 coating, is worth of further investigation.

4. Conclusion

We report the microstructural and electrochemical properties of MgH_2 and $\text{MgH}_2\text{-C}$ films for lithium ion battery anode. The as-deposited MgH_2 and $\text{MgH}_2\text{-C}$ films by RF magnetron sputtering have nanocrystalline structure and reversible lithium storage properties through conversion reaction of MgH_2 with lithium, the equilibrium discharge potential of MgH_2 film was determined to be 0.55 V vs. Li/Li^+ . In comparison with MgH_2 film, the $\text{MgH}_2\text{-C}$ film shows improved polarization effect in the first discharge and microstructural stability during cycling. Unfortunately, both MgH_2 and $\text{MgH}_2\text{-C}$ films show poor cyclic performance, which is mainly due to the low reversibility of Mg/LiH in the delithiation process. To improve the cyclic life of MgH_2 film electrode, a protective coating with proper composition and nanostructure might avoid the loss of LiH and promote the reversible formation of MgH_2 , and such research effort is ongoing.

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Figure captions

Fig. 1. Schematic illustration of Mg-C composite target.

Fig. 2. XRD patterns of as-deposited Mg film (a) and Mg-C film (c), as-hydrogenated Mg film (b) and Mg-C film (d), with the Si wafer substrate.

Fig. 3. SEM images showing the surface morphologies of Mg film (a) and MgH₂ film (b), Mg-C film (c) and MgH₂-C film (d), with the Cu foil substrate. (e): the elemental mapping for MgH₂-C film.

Fig. 4. Electrochemical performances of MgH₂ film electrode: (a) First discharge and charge voltage profiles at 12 $\mu\text{A cm}^{-2}$ in the voltage range 0.01-2.0 V, (b) CV curves tested with the cutoff voltage 0.01-2.0 V at 0.2 mV s^{-1} , (c) GITT curve recorded in the first discharge and charge cycle. The inset shows the voltage hysteresis, (d) Cyclic discharge/charge voltage profiles at 12 $\mu\text{A cm}^{-2}$ and in the voltage range 0.2-2.0 V, the first discharge capacity was limited to 150 μAh .

Fig. 5. Electrochemical performances of MgH₂-C film electrode: (a) First discharge and charge voltage profiles at 12 $\mu\text{A cm}^{-2}$ in the voltage range 0.01-2.0 V, (b) CV curves tested with the cutoff voltage 0.01-2.0 V at 0.2 mV s^{-1} , (c) Cyclic discharge/charge voltage profiles at 12 $\mu\text{A cm}^{-2}$ in the voltage range 0.2-2.0 V, and the first discharge capacity was limited to 80 μAh (d) Nyquist plots of half-cells at the discharge potential of 0.2 V in various cycles.

Fig. 6. SEM images showing the surface morphology of MgH₂ (a) and MgH₂-C (b) film electrodes after 10 cycles.