



Short communication

Carboxymethylcellulose and carboxymethylcellulose-formate as binders in MgH₂–carbon composites negative electrode for lithium-ion batteries

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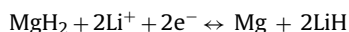
ABSTRACT

Influence of carboxymethylcellulose sodium salt (CMC) and carboxymethylcellulose-formate (CMC-f) binders on the cyclability of a MgH₂–33.3% CMC type binder–33.3% C_{tx} electrodes has been investigated for the first time. These electrodes show a large reversible capacity of 1800–1900 mAh g⁻¹ at an average voltage of 0.5 V vs. Li⁺/Li⁰ which is suitable for the negative electrode in lithium-ion batteries. Moreover, addition of CMC or CMC-f binder with C_{tx} carbon leads to an improved capacity retention with 240 mAh g⁻¹ and 542 mAh g⁻¹, respectively, compare to 174 mAh g⁻¹ for MgH₂–18% C_{tx} after 40 cycles.

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1. Introduction

Recently, the use of metal hydrides (MgH₂) as negative electrode for Li-ion technologies has been demonstrated as a promising route for energy storage [1,2]. The MgH₂ optimized electrode shows a large reversible capacity of 1480 mAh g⁻¹ (four times that of conventional Li/C electrodes) at an average voltage of 0.5 V vs. Li⁺/Li⁰. In addition, the polarization shows the lowest value (0.2 V vs. Li⁺/Li⁰) ever reported for conversion electrodes. The discharge electrochemical reaction results in the formation of a composite made of Mg particles embedded in a LiH matrix, which on charging converts back to MgH₂. The general mechanism for the reaction is:



Though quite attractive, limitations of the performances of the MgH₂ electrode due to a slow hydrogen diffusion appears at high cycling rate as well as a capacity fading in relation with the poor electronic conductivity of the active material (MgH₂ or LiH + Mg mixture) and the large volume variation of the electrode during the repeating charge/discharge cycles.

This volume variation of 83% between MgH₂ (61.59 Å³) and Mg (46.46 Å³) + 2 LiH (2 × 33.3 Å³) is at the origin of the cycling degradation in relation with the loss of electronic percolation within the electrode inherent to the MgH₂ conversion reaction.

To accommodate the volume expansion limitation and consequently to enhance the cycling behavior, the use of sodium carboxymethylcellulose (CMC) [3,4] as a potential binder has been widely studied in the case of silicon electrodes [5–16]. This stiff polymer surprisingly sustains the 270% volume change occurring at the electrode during cycling. Within the numerous works devoted to understand this behavior different ideas came up to explain the improved capacity retention of the Si–CMC–C electrode. The first ones are linked with the existence of some chemical or physical interactions between CMC binder and Si particle surfaces, enabling a reversible reaction of Si with Li (a chemical condensation between acetate function of CMC and silicic acid [12] or hydrogen bonds [9]). In contrast, Lestriez et al. [8] implies that it is more a physical cross-linking with an efficient networking process between carbon conductive agent and silicon due to the extended conformation of CMC in solution which helps to preserve the conductivity of the electrode. With respect to a geometrical model, Beattie et al. [10] estimate the amount of CMC binder needed to accommodate the volume variation of the electrode, and show that low Si content <33% and high binder content between 33% and 56% cycle at large capacity.

Pursuing these concepts, the effect of the addition via a solid state route of CMC and of a CMC derivative, carboxymethylcellulose-formate (CMC-f) [17], on the cyclability of MgH₂–carbon electrode was studied. In addition to carboxymethyl and free OH groups present into the CMC polymer chain, CMC-f possess formyl ester groups. Consequently, CMC-f is a less ionic polymer formylation making this polymer more lipophilic. The aim of this work is thus to study the effect of the

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CMC polymer structure modification onto the electrochemical cell properties and to show than CMC type binder are able to accommodate the volume variation of the electrode.

2. Experimental

MgH₂ is prepared by ball milling for 2 h of Mg powder (Aldrich) mixed with 18% of preground C_{t,x} carbon with a Spex 8000 mixer-mill, where *t* and *x* refers to the pregrinding time (*t* = 7 h) and the resulting Brunauer–Emmett–Teller (BET) surface area of the carbon (*x* = 460 m² g⁻¹), respectively. The C_{7,460} carbon used to prepare the Mg–18% C_{t,x} mixture is obtained by ball-milling during 7 h of MCMB 25–28 graphite (e.g. mesocarbon microbeads having 25 μm in diameters and fired at 2800 °C) previously degassed under primary vacuum. Afterwards this Mg–18% C_{t,x} mixture was hydrogenated at 350 °C for 10 h under 20 bars of hydrogen pressure via a solid–gas reaction in a stainless-steel vessel, and subsequently ball milled a second time before being used as electrode material.

Carboxymethyl cellulose (CMC) (ACROS Organics, molecular weight Mw = 700000, degree of substitution DS = 0.9) was dried at 100 °C under primary vacuum during 10 h prior to use as binder in the MgH₂ electrode. Carboxymethylcellulose-formate is also dried previously to use in the same way. FTIR spectra are performed with a SHIMADZU 8400S spectrophotometer in the 600–4000 cm⁻¹ frequency range equipped with an attenuated total reflectance probe (ATR).

Two mixtures of MgH₂, CMC or CMC-f and carbon C_{7,460} with the respective weight ratio of 33.3%, 33.3%, 33.3% were ground 2 h using a Spex 8000 mixer mill under argon in a 25-ml stainless steel milling container with a ball to powder weight ratio of 10.

Swagelok-type cells were assembled in an argon filled glove box and cycled using a Mac pile automatic cycling/data recording system (Biologic Co, Claix, France) operating in galvanostatic mode between 3 V and 0.005 V vs. Li⁺/Li⁰. These cells comprise (1) a 1-cm², 75-μm-thick disk of composite positive electrode containing 7 mg of MgH₂ mixed with CMC or CMC-f and carbon, (2) a 1-cm² Li metal disk as the negative electrode, and (3) a Whatman GF/D borosilicate glass fibre sheet saturated with a 1 M LiPF₆ electrolyte solution in 1:1 dimethyl carbonate:ethylene carbonate as separator/electrolyte. The cells were cycled at a rate of one lithium in 10 h. The reversible capacity of the cell is defined as the capacity difference between the discharge and the charge.

The current density of the C_{t,x} carbon denoted *J*_{C_{t,x}} is calculated from experimental electrochemical data obtained on a C_{t,x} carbon electrode. The C_{t,x} carbon electrode presents a reversible capacities of 400, and 40 mAh g⁻¹ at the first and 40th cycle, respectively. That of MgH₂ denoted *J*_{MgH₂} is equal to *J*_{electrode} - *J*_{C_{t,x}} where *J*_{electrode} is the experimental current density of the electrode. The current efficiency ε_{MgH₂} is equal to *J*_{MgH₂} / (*J*_{MgH₂} + *J*_{C_{t,x}}) and the surface of the electrode is estimated around 1 cm².

3. Results and discussion

3.1. Carboxymethylcellulose-formate synthesis and characterization

Carboxymethylcellulose-formate is synthesized from the commercial CMC according to the method introduced by Heinze et al. [17]. Formate functionalization is proved by FTIR spectroscopy with the development of a vibration band at 1718 cm⁻¹ characteristic of formyl ester groups (lit. 1725 cm⁻¹ [17]) (Fig. 1b). Preservation of carboxymethyl group grafted onto the polymer backbone is also demonstrated by the persistence of the corresponding 1600 cm⁻¹ characteristic vibration band, already present in CMC (lit. 1607 cm⁻¹ [17]) (Fig. 1a and b). From the presence of

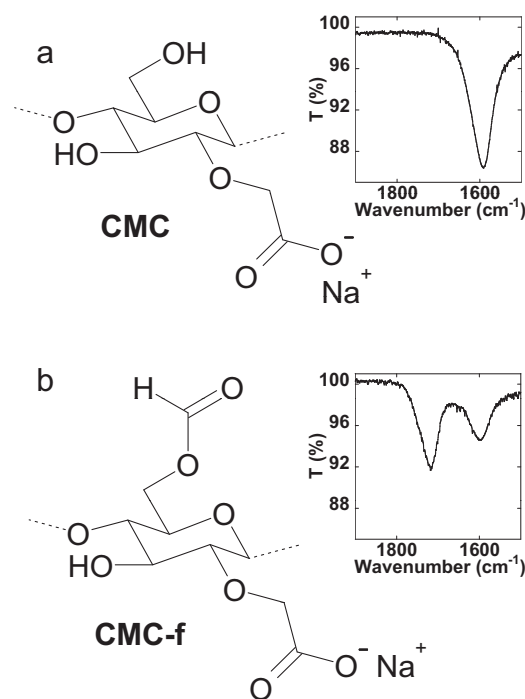


Fig. 1. Molecular structure and corresponding IRTF spectra of sodium carboxymethylcellulose (CMC) (a) and carboxymethylcellulose-formate (CMC-f) (b).

a broad signal at 3000–3600 cm⁻¹ it can be concluded that it also remains some free OH groups in this polymer.

3.2. Reactivity of MgH₂ with lithium ion

The potential vs. Li composition (i.e. *y* = moles fraction of Li) profiles for MgH₂–18% C_{t,x}/Li MgH₂–33.3% (CMC)–33.3% C_{t,x}/Li and MgH₂–33.3% (CMC-f)–33.3% C_{t,x}/Li cells discharged at a current of one lithium for 10 h between 3 V and 0.005 V are shown in Fig. 2. For the MgH₂–18% C_{t,x}/Li composite electrode cell, initial potential abruptly drops to reach a first plateau located near 0.8 V and a second one at 0.44 V prior to showing another fast decay around *y* = 1.5 to reach a lower voltage plateau (near 0.095 V) that extends up to *y* = 2.3. The electrochemical reactions involved here have been previously demonstrated by ex situ XRD diffraction from different *y* values to be a lithium driven conversion reaction: MgH₂ + 2Li⁺ + 2e⁻ ↔ Mg + 2LiH at 0.44 V and a Mg–Li alloying reaction above *y* = 1.7 [1,2]. The MgH₂–18% C_{t,x}/Li electrode shows a large reversible capacity of 1700 mAh g⁻¹ for an irreversible loss around 25%.

A C_{t,x} carbon amount increase, from 18% to 33.3% (Fig. 2), leads to an irreversible loss rise (from 25% to 39%) which is due to the electrolyte decomposition on high BET surface area C_{t,x} carbon. This is concomitant with the length of the plateau at 0.8 V. More interestingly, the reversible capacity of the MgH₂ active material is not affected by an increase of additive amount (C_{t,x} or CMC). Capacities of 1800 mAh g⁻¹ and 1900 mAh g⁻¹ are indeed obtained for the MgH₂–33.3% (CMC)–33.3% C_{t,x}/Li and MgH₂–33.3% (CMC-f)–33.3% C_{t,x}/Li cells, respectively.

Cycling behavior for MgH₂ composite electrodes, i.e. evolution of the cell reversible capacity according to the cycle number is shown in Fig. 3. Aside from a drastic decrease of the reversible capacity occurring for the five first cycles, a much better capacity retention is obtained for the MgH₂–33.3% C_{t,x} electrodes containing the CMC or CMC-f binders compared to MgH₂–18% C_{t,x}. Moreover, a better behavior is noticed for the electrode containing the CMC-f binder compared to the one with CMC binder. Capacities of

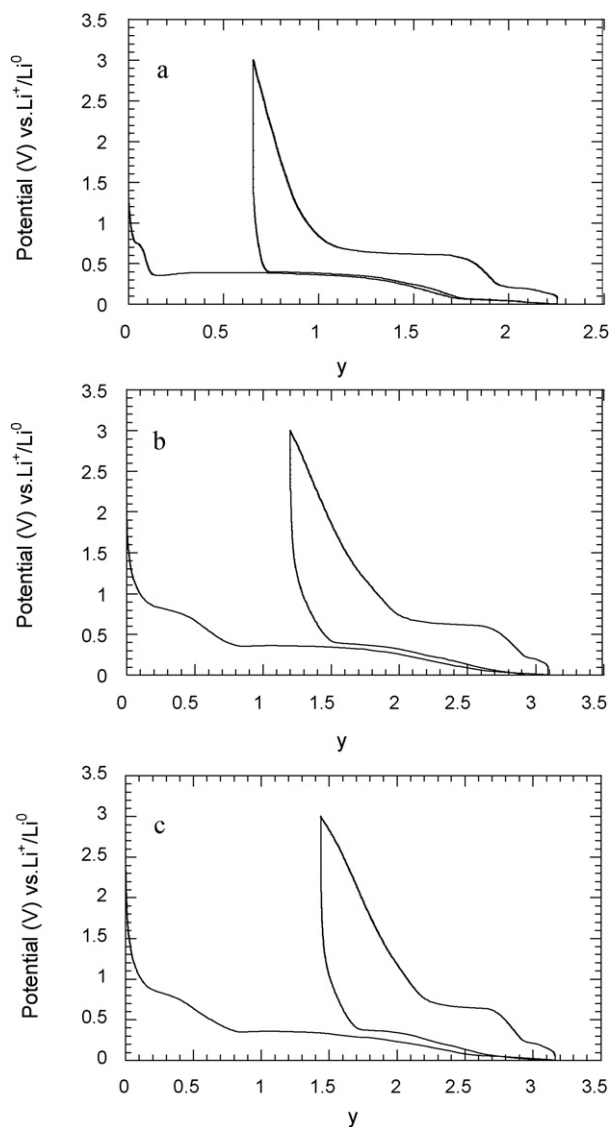


Fig. 2. Evolution of the potential (V) as a function of y (i.e. moles fraction of Li) for MgH_2 electrodes cycled between 3 and 0.005 V at a rate of one lithium in 10 h: (a) MgH_2 -18% $\text{C}_{t,x}$ (b) 33.3% MgH_2 -33.3%(CMC)-33.3% $\text{C}_{t,x}$ (c) 33.3% MgH_2 -33.3%(CMC-f)-33.3% $\text{C}_{t,x}$.

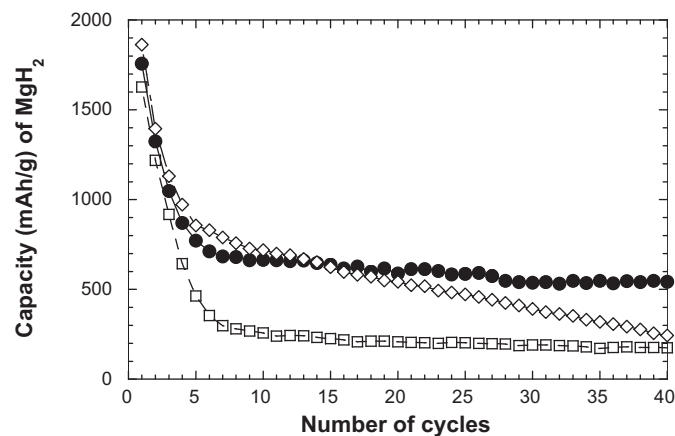


Fig. 3. Cycling performance for MgH_2 composite electrodes: MgH_2 -18% $\text{C}_{t,x}$ (empty squares), 33.3% MgH_2 -33.3%(CMC)-33.3% $\text{C}_{t,x}$ (empty diamonds) and 33.3% MgH_2 -33.3%(CMC-f)-33.3% $\text{C}_{t,x}$ (solid circles) (cycling between 3 and 0.005 V, rate of one lithium in 10 h).

Table 1

Current efficiencies $\varepsilon_{\text{MgH}_2}$ for MgH_2 in MgH_2 -18% $\text{C}_{t,x}$, MgH_2 -33% $\text{C}_{t,x}$ -33%CMC and MgH_2 -33% $\text{C}_{t,x}$ -33%CMC-f electrodes.

Current efficiency ε of MgH_2	MgH_2 -18% $\text{C}_{t,x}$	MgH_2 -33% $\text{C}_{t,x}$ -33%CMC	MgH_2 -33% $\text{C}_{t,x}$ -33%CMC-f
Cycle n 1	95%	79%	77%
Cycle n 40	95%	83%	93%
% of $\text{C}_{t,x}$ carbon in each electrode	18%	33%	33%

240 mAh g^{-1} and 542 mAh g^{-1} are indeed obtained at the 40th cycle for the CMC and CMC-f binders, respectively, in comparison to a value of 174 mAh g^{-1} without any binder.

Using a simple arithmetic approach, the capacity contribution of the $\text{C}_{t,x}$ carbon has been estimated from the capacity of a $\text{C}_{t,x}$ electrode to be 200 and 20 mAh g^{-1} at the first cycle and the 40th cycle, respectively. Within this speculation, there is no doubt than the better capacity retention after 40 cycles for the MgH_2 -33% $\text{C}_{t,x}$ -33%CMC electrode cannot be attributed to an additional capacity of 20 mAh g^{-1} coming from the $\text{C}_{t,x}$ carbon. The corresponding current efficiencies for the MgH_2 -33% $\text{C}_{t,x}$ -33%CMC and the MgH_2 -33% $\text{C}_{t,x}$ -33%CMC-f electrodes are 83% and 93%, respectively, after 40 cycles (Table 1).

It must be emphasized that this behavior is not in relation with the carbon amount increase since no cycling behavior improvement have been noticed for the MgH_2 -33.3% $\text{C}_{t,x}$ mixture and than different capacities values are measured for electrodes having the same amount of carbon.

This is a rather promising result because optimized efficiency of the CMC binder is usually obtained when the active material is mixed with an aqueous CMC solution, enabling in this way an intimate mixture of the active components.

Moreover, cycling performance enhancement observed here when CMC-f is used in place of CMC, could be explained because CMC-f is a less ionic, more hydrophobic polymer. Consequently, different kind of interactions could come into play and a better mixing of CMC-f with MgH_2 and $\text{C}_{t,x}$ could be obtained during solid mixing.

Another conceivable hypothesis could be a simple volume effect, i.e. a different porosity between CMC and CMC-f composite electrodes. Recently, Guo et al. [11] achieve the synthesis of a CMC scaffold-nanoSi electrode, demonstrating the crucial importance of the porosity of CMC in the cycle stability and energy and power density. It must also be emphasized here that a polymer chain length decrease caused by the aggressive medium used for chemical modification (formic acid), can not be totally excluded even if it is assumed to be light. This modification could have an advantageous effect onto the cyclability, still due to a better mixing of the components.

Further characterization of these materials, especially by IRTF and NMR spectroscopies, transmission electronic microscopy (TEM) and differential scanning calorimetry (DSC) are currently under study. With these complementary experiments we will be able to draw some conclusions, especially to determine if the observed improvement is in relation with the existence of a chemical interaction between CMC-f type binder and MgH_2 or $\text{C}_{t,x}$ or simply a volume effect.

4. Conclusion

The addition of CMC binders in the magnesium hydride electrode has been experimentally investigated. The MgH_2 electrodes mixed with CMC binders preserve important initial reversible capacities at the first cycle of 1800 mAh g^{-1} and 1900 mAh g^{-1} for the MgH_2 -33.3%(CMC)-33.3% $\text{C}_{t,x}$ /Li and MgH_2 -33.3%(CMC-f)-33.3% $\text{C}_{t,x}$ /Li cells, respectively. Despite an important capacity

decrease during the five first cycles, an interesting effect on the retention capacity is noticed for CMC-f with 560 mAh g^{-1} obtained after 40 cycles. Thus, further development of MgH_2 electrode containing nanopowders or nanofibers is needed to sustain full capacity of the MgH_2 in a conversion process.

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