Electrochimica Acta 277 (2018) 20–29

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrochemical and structural investigations of different polymorphs of TiO_2 in magnesium and hybrid lithium/magnesium batteries

Qiang Fu [a, *], Raheleh Azmi [a], Angelina Sarapulova [a], Daria Mikhailova [a, c], Sonia Dsoke [a, b], Aleksandr Missiul [e], Vanessa Trouillet [a, d], Michael Knapp [a, b], Natalia Bramnik [a], Helmut Ehrenberg [a, b]

[a] Institute for Applied Materials (IAM), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344, Eggenstein-Leopoldshafen, Germany
[b] Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Helmholtzstrasse 11, 89081, Ulm, Germany
[c] Leibniz Institute for Solid State and Materials Research (IFW) Dresden e.V., Helmholtzstraße 20, D-01069, Dresden, Germany
[d] Karlsruhe Nano Micro Facility (KNMF), Karlsruhe Institute of Technology (KIT), 76344, Eggenstein-Leopoldshafen, Germany
[e] CELLS-ALBA Synchrotron, E-08290, Cerdanyola del Valles, Barcelona, Spain

ARTICLE INFO

Article history:
Received 16 February 2018
Received in revised form
19 April 2018
Accepted 26 April 2018
Available online 27 April 2018

Keywords:
TiO_2
Hybrid lithium/magnesium batteries
In situ synchrotron
X-ray photoelectron spectroscopy (XPS)
Electrochemical performance

ABSTRACT

Commercial nanocrystalline TiO_2 anatase and self-prepared TiO_2(B) bronze synthesized by hydrothermal method were used as the cathode materials for Mg-ion and hybrid Li/Mg-ion batteries. The TiO_2 anatase delivers high initial discharge/charge capacities of 225 mAh g^{-1}/204 mAhg^{-1} in a mixture of Phenylmagnesium chloride-$AlCl_3$/LiCl in tetrahydrofuran (APC/LiCl) hybrid electrolyte, while the TiO_2(B) shows high initial discharge/charge capacities of 260 mAh g^{-1}/231 mAh g^{-1} in the same hybrid electrolyte. Low discharge capacities of 67 and 57 mAh g^{-1} and strong polarization are observed for both TiO_2 anatase and TiO_2(B) samples in pure APC electrolyte, respectively. *In situ* synchrotron diffraction strongly identifies that in APC/LiCl hybrid electrolyte, the TiO_2 anatase undergoes structural evolution via a solid solution and a two-phase reaction mechanism, while TiO_2(B) exhibits a solid solution reaction during the discharge-charge processes. The analysis of X-ray photoelectron spectra for the TiO_2 anatase and TiO_2(B) cathodes in the discharged/charged states reveals a change of Mg/Ti as well as Li/Ti ratios at different stages, which may indicate a contribution of both Mg and Li to the charge storage mechanism in the hybrid electrolyte.

1. Introduction

Owing to their high energy density and long cycle lifetime, Lithium-ion batteries (LIBs) are widely used in portable electronics and mobile phones. But their applications are limited in electric vehicles and stationary energy storage because of high cost and safety concerns [1–3]. Mg-ion batteries (MIBs) have recently attracted extensive attention worldwide, due to their potential advantages compared with LIBs, such as higher volumetric energy density, lower cost, and higher safety [4–7]. However, the magnesium-ion batteries are far from being commercialized, since the promising system consisting of high-performance electrode materials and compatible non-aqueous magnesium electrolyte is still lacking. The development of magnesium-insertion electrode materials is particularly difficult due to the intrinsic sluggish transport of Mg^{2+}-ions in solids. This problem can be overcome in the Li^+/Mg^{2+} hybrid ion battery (LMIB) which combines a lithium-insertion host cathode, metallic magnesium anode, and Li^+/Mg^{2+} non-aqueous hybrid electrolyte [8,9]. During cycling of the battery, the cathode reaction is dominated by Li^+ intercalation/de-intercalation processes [8], with a small proportion contribution of Mg^{2+} storage, whereas only Mg deposition/dissolution occurs on the anode side to ensure the high safety of these batteries. Therefore, various Li^+ insertion compounds can be used as cathode materials providing that the operation voltage of the cathode under consideration falls in the electrochemical stability range of the electrolyte. However, the development of magnesium electrolytes, which are compatible with metallic magnesium and suitable for high-voltage cathodes is a challenging task. It should be pointed out

* Corresponding author.
E-mail address: qiang.fu@kit.edu (Q. Fu).

https://doi.org/10.1016/j.electacta.2018.04.200
0013-4686/

that current Li^+/Mg^{2+} hybrid electrolytes formulations reported so far in literature such as $Mg(BH_4)_2$+$LiBH_4$/tetraglyme (TG) [10] and $(PhMgCl)_2$-$AlCl_3$+LiCl/$LiBH_4$/tetrahydrofuran (THF) [8,9,11,12] are not stable at voltages higher than 2.5 V vs Mg^{2+}/Mg [13–15]. So far, only a few of materials such as TiO_2, TiS_2, $Li_4Ti_5O_{12}$, Mo_6S_8 and MoS_2 et al. [8,10,12,16–19], have been studied for positive electrode in LMIBs. These LMIBs show outstanding electrochemistry performance because of the facile Li^+ ions migration in the materials.

Several structural modifications of TiO_2 [20–22] are well known as lithium-insertion compounds with insertion potentials of 1.5–1.7 V vs Li^+/Li. These compounds are considered as promising anode materials for Li-ion batteries due to their long cycle stability, low cost, and environmental friendliness. Recently, Nuli et al. reported the good performance of a hybrid Li^+/Mg^{2+} cell with nanocrystalline anatase TiO_2 and nanocrystalline TiO_2(B) as cathode materials [10,16], where the TiO_2 anatase delivered an initial discharge/charge capacity of 156/147 $mAhg^{-1}$ at 0.2C rate and TiO_2(B) of 254/214 $mAhg^{-1}$ at 0.1C rate. The co-intercalation of Li^+ and Mg^{2+} into TiO_2-anatase during operation of the cell with Mg-anode and $LiBH_4$-$Mg(BH_4)_2$/tetraglyme electrolyte was proposed [10], although only minor changes in diffraction patterns of the TiO_2 anatase in the hybrid electrolyte were reported. The structural evolution of the TiO_2 anatase during operation in the mixed Li/Mg electrolyte seems to be quite different compared to the well-established mechanism of lithiation-delithiation in standard lithium electrolytes [23]. Recently, the poor electrochemical performance of TiO_2 anatase in pure Mg-ion ("All phenyl" complex solution, APC) electrolyte was reported [24], which was consistent with only minor changes in the lattice parameters between the pristine and discharged TiO_2 anatase. For a TiO_2(B) cathode, a pseudocapacitive reaction mechanism was reported in a $LiBH_4$-$Mg(BH_4)_2$/tetraglyme and APC-LiCl hybrid electrolyte [12,16]. *In situ* synchrotron powder diffraction is a powerful technique to study the structural evolution of battery materials [25,26]. To the best of our knowledge, it has been not yet applied for study of both TiO_2 materials in hybrid LMIBs.

The crystal structure of TiO_2 anatase has a tetragonal body-centered space group $I4_1/amd$. It is comprised of TiO_6 octahedra sharing edges with four adjacent TiO_6 octahedra so that infinite planar double chains are formed as shown in Fig. 1a. There are vacant octahedral and tetrahedral sites between the TiO_6 octahedra, that can be occupied by the guest cations. It has been reported that Li-ion insertion occurs into the octahedral sites [27]. On the other side, the crystal structure of TiO_2(B), as shown in Fig. 1b, is monoclinic with space group $C2/m$ and is formed with edge and corner-sharing TiO_6 octahedra with an open channel parallel to the *b*-axis, which could be accessible for alkali and earth alkali cations [28]. In this work, we study the electrochemical performance of two TiO_2 modifications, namely, TiO_2-anatase and TiO_2(B), in APC/LiCl hybrid electrolytes. The evolution of the crystal structure for both TiO_2 types was studied by *in situ* synchrotron diffraction and the cathode surface was characterized by *ex situ* X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Preparation of TiO_2(B) nanowires

TiO_2 anatase nanopowder (99%, particle size <25 nm) was purchased from Sigma-Aldrich. TiO_2(B) nanowires were synthesized by the hydrothermal method [29]. Initially, 0.8 g of TiO_2 (P25, 99.9%, Sigma-Aldrich) were dispersed in NaOH solution (80 mL, 10 M). After ultrasonic treatment and stirring, the resulting suspension was transferred into the autoclave. The autoclave was then sealed and heat-treated at 170 °C for 60 h. The obtained white powder was washed by constant stirring in 0.1 M of HCl solution for 8 h. The obtained hydrion exchanged titanate precipitate was then centrifuged and washed three times with deionized water. The solid product was dried at 80 °C overnight. After that, the titanate precipitate was annealed at 400 °C for 4 h in air to obtain the TiO_2 nanowires.

Chemical insertion of magnesium into TiO_2 anatase and TiO_2(B) was performed at room temperature by stirring TiO_2 with Di-*n*-butylmagnesium ($[CH_3(CH_2)_3]_2Mg$) solution (molar ratio of TiO_2:MgC_8H_{18} = 1:2) for one week in heptane under Ar.

2.2. Preparation of hybrid electrolytes

The preparation of electrolytes was performed in an argon-filled glove box with H_2O and O_2 contents less than 2 ppm "All phenyl" complex (APC) electrolyte was prepared by dissolving corresponding amounts of 2 M Phenylmagnesium chloride in tetrahydrofuran ($(PhMgCl)_2$/THF) and $AlCl_3$ in THF to get 0.4 M $(PhMgCl)_2$-$AlCl_3$. The ACP/LiCl hybrid electrolyte was prepared by dissolving stoichiometric 2 M $(PhMgCl)_2$/THF, $AlCl_3$ and LiCl in tetrahydrofuran (THF) to produce 0.4 M $(PhMgCl)_2$-$AlCl_3$/0.4 M LiCl/THF. All the chemicals for 2 M $(PhMgCl)_2$/THF, $AlCl_3$, LiCl, and THF are water free from Sigma-Aldrich without any further drying.

2.3. Morphological and structural characterization

The morphology of the particles was studied with a Zeiss Supra 55 Scanning Electron Microscope (SEM). The structural characterizations were performed using synchrotron radiation (λ = 0.4129 Å) at the powder diffraction beam line MSPD at the synchrotron ALBA (Barcelona, Spain) [30]. For ex-situ characterization, the powder samples were filled in 0.5 mm Ø glass capillaries. The details of the *in situ* setup can be found elsewhere [26]. The diffraction data were analyzed by Rietveld method using the Fullprof software package [31]. X-ray photoelectron spectroscopy

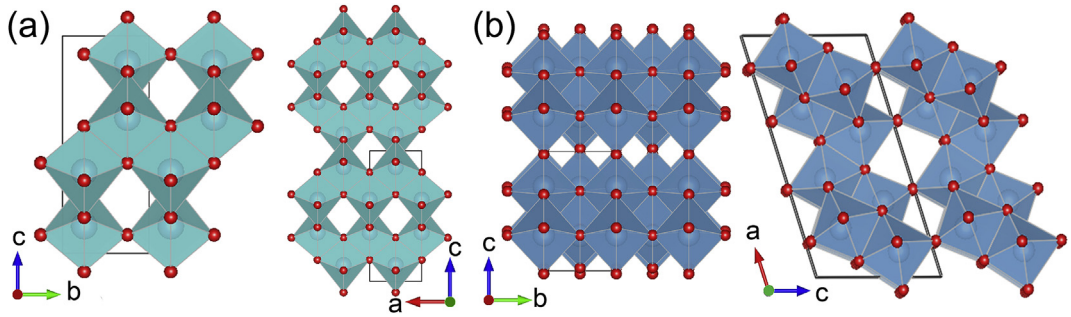

Fig. 1. Crystal structures of both TiO_2 Anatase (a) and TiO_2(B) (b).