Journal of Power Sources 384 (2018) 18–26

Contents lists available at ScienceDirect

Journal of Power Sources

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

Surface and interface engineering of anatase TiO_2 anode for sodium-ion batteries through Al_2O_3 surface modification and wise electrolyte selection

Tao Li[a,b,**], Umair Gulzar[a,b], Xue Bai[a,c], Simone Monaco[a], Gianluca Longoni[a], Mirko Prato[a], Sergio Marras[a], Zhiya Dang[a], Claudio Capiglia[d,e], Remo Proietti Zaccaria[a,f,*]

[a] *Istituto Italiano di Tecnologia, Via Morego 30, Genova 16163, Italy*
[b] *Department of Informatics, Bioengineering, Robotics and Systems Engineering (DIBRIS), University of Genova, Via Dodecaneso 35, Genova 16146, Italy*
[c] *Key Laboratory for Liquid – Solid Structural Evolution & Processing of Materials (Ministry of Education), Shandong University, Jinan 250061, China*
[d] *Recruit R&D Co., Ltd., Recruit Ginza 8 Bldg. 8-4-17, Ginza Chuo-Ku, Tokyo 104-8001, Japan*
[e] *Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Aichi, 466-8555, Japan*
[f] *Cixi Institute of Biomedical Engineering, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Science, Ningbo 315201, China*

HIGHLIGHTS

- Al_2O_3 coating of nanostructured TiO_2 for sodium-ion batteries.
- Influence of different $NaClO_4$-based solvents.
- Surface and interface engineering.

ARTICLE INFO

Keywords:
Sodium-ion batteries
Nanostructured TiO_2
Al_2O_3 surface coating
Interface engineering
Anode material

ABSTRACT

In the present study, Al_2O_3 is utilized for the first time as coating agent on nanostructured anatase TiO_2 in order to investigate its effect on sodium-ion batteries performance. Our results show that the Al_2O_3 coating, introduced by a facile two-step approach, provides beneficial effects to the TiO_2-based anodes. However, the coated TiO_2 still suffers of capacity fading upon cycling when using 1.0 M of $NaClO_4$ in propylene carbonate (PC) as electrolyte. To address this issue, the influence of different electrolytes ($NaClO_4$ salt in various solvents) is further studied. It is found that the modified TiO_2 exhibits significant improvements in cycling performance using binary ethylene carbonate (EC) and PC solvent mixture without the need of the commonly used fluoroethylene carbonate (FEC) additive. Under the best configuration, our battery could deliver a high reversible capacity of 188.1 mAh g^{-1} at 0.1C after 50 cycles, good rate capability up to 5C, and remarkable long-term cycling stability at 1C rate for 650 cycles. This excellent performance can be ascribed to the synergistic effects of surface and interface engineering enabling the formation of a stable and highly ionic conductive interface layer in EC:PC based electrolyte which combines the native SEI film and an ‘artificial’ SEI layer of irreversibly formed Na – Al – O.

1. Introduction

The progressive and inevitable depletion of fossil fuels and the increasing demand for renewable energy sources has led the scientific community to turn its attention towards efficient electrochemical energy storage systems. In this regard, lithium-ion batteries (LIBs) are recognized as one of the most prominent technologies, with their performance on a steady improvement since its first advent in 1991 [1,2]. However, the high price and non-uniform distribution of lithium-containing natural resources has stimulated the investigation of sodium-ion batteries (SIBs), due to the natural abundance of sodium precursor in the lithosphere and to the lower manufacturing costs [3,4]. These aspects are of foremost importance in favouring the penetration of SIB technology in the mid-to large-scale stationery storage and the automotive sectors [5–7]. Despite SIBs have been regarded as a promising candidate in replacing LIBs in many applications where the reduction of investment costs are of primarily importance, they still carry a number of intrinsic drawbacks. Most notably, the sluggish ion diffusion and the volume expansion during cycling caused by the large radius of Na^+ (0.102 nm, about 35% higher than Li^+ radius) have been leading to

---

[*] Corresponding author. Cixi Institute of Biomedical Engineering, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Science, Ningbo 315201, China.
[**] Corresponding author. Istituto Italiano di Tecnologia, via Morego 30, Genova 16163, Italy.
E-mail addresses: Tao.Li@iit.it (T. Li), Remo.Proietti@iit.it, Remo.Proietti@nimte.ac.cn (R. Proietti Zaccaria).

https://doi.org/10.1016/j.jpowsour.2018.02.052
Received 18 November 2017; Received in revised form 3 February 2018; Accepted 18 February 2018

unsatisfactory electrochemical performance [7,8] therefore pushing for the identification of suitable host materials for sodium storage.

In this regard, with respect to the anode, hard carbon takes up this hot challenge owing to its outstanding storage capability of sodium ions. However, it is also characterized by a poor cycling rate, caused by the limited diffusion coefficient of sodium in carbon [9–11], as well as by safety issues due to its low operation potential occurring close to sodium plating [11]. Besides hard carbon, high capacity materials such as alloy based materials (e.g. Sn [12–14], Sb [15–17], Ge [18,19]) and phosphorus [20,21] have been considered for SIBs, even though their large volume expansion during sodiation-desodiation limits their electrochemical performance. By contrast, TiO_2 with the merits of low cost, environmental friendliness, intrinsic safety and negligible volume variation has been intensively explored as a promising anode material for secondary batteries [22–25]. Especially for SIBs [9,22,23], the most electrochemically active polymorphs of TiO_2 is considered to be anatase owing to its suitable Na^+ diffusion pathways and abundance of sites for Na^+ insertion. However, it still suffers the shortcomings of low electronic and ionic conductivity [9]. Therefore, these critical issues have to be addressed before the practical application of TiO_2 within SIBs can become reality.

To date, various strategies have been proposed to improve the conductivity of active materials. Nanostructuring and surface modification are, for instance, effective solutions. In particular, active surface engineering achieved by downsizing the particles dimension to the nanometer scale benefits the reduction of ionic migration and electronic path length [26,27]. Contemporary, it also results in the realization of electrode materials with larger active surface area [9,22]. With respect to the interface engineering through surface modification, it has been suggested that the coating of TiO_2 with carbon materials could effectively separate it from the caustic electrolyte so to suppress undesirable interfacial side reactions, alleviate the decomposition of electrolytes, and enhance the electronic conductivity of the electrode [22,23,28–32]. Besides carbon materials, solid electrolytes, oxides and metal fluorides have been actively employed for the surface modification of LIBs cathode and anode. Indeed, coatings realized by employing these electrochemically less active non-carbon compounds do not simply effectively suppress any undesired interfacial side reaction but they also improve ionic conductivity, structural reversibility, and reliability of the electrode. Furthermore, with respect to the common strategies used for carbon coating, it is more feasible to realize uniform non-carbon coatings due to an easier thickness control. Specific examples are Al_2O_3-coated $LiCoO_2$ [33–35], Al_2O_3-coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ [36], Li_2SiO_3-coated $Li_{1.13}Ni_{0.30}Mn_{0.57}O_2$ [37], AlF_3-coated $Li[Li_{0.19}Ni_{0.16}Co_{0.08}Mn_{0.57}]O_2$ [38], Al_2O_3-coated $Li_4Ti_5O_{12}$ [39,40] and silicon [41,42], while reports on adopting non-carbon coating materials to modify SIBs positive or negative electrodes are still very scarce.

In particular, LIBs oriented electrode materials modified by Al_2O_3 coating using various methods such as physical vapour deposition (PVD), vapour-assisted hydrolysis technique, atomic layer deposition (ALD), radio frequency magnetron sputtering method and sol-gel processing have showed enhanced capacity retention and rate capability [33–36,39–42]. The reason is generally explained by the improved structural stability of the electrode, an effective surface protection capable of preventing electrolyte side reactions, and improved electrode/electrolyte interface properties owing to the formation of $Li-Al-O$ solid solution phase coating characterized by high Li^+ ion conductivity. Similarly, when it comes to the study of Al_2O_3 coating in emerging SIBs, in 2013 Han et al. [43] investigated the effect of an Al_2O_3 atomic layer deposition on the cycling performance of a hybrid anode of Sn nanoparticles attached on carbon nanofibers (SnNPs@CNF). Their results revealed that the ALD-Al_2O_3 coating (6 nm thick) remarkably boosted the cycling performance of the Sn anode. This effect was attributed to the unique features of the $Na-Al-O$ layer, being it irreversibly formed after the reaction between the Al_2O_3 coating and Na^+, similarly to the lithiation process occurring with Al_2O_3. The in situ TEM study confirmed the irreversible conversion from Al_2O_3 coating to $Na-Al-O$ structure in the first sodiation stage. The authors concluded that the $Na-Al-O$ layer acts not only as an ion transport channel for Na^+ diffusion but also as a stretchable mechanical protection layer to buffer the severe volume changes of Sn under charging/discharging process. Jung et al. [44] reported about sodiation and lithiation processes in Al_2O_3 using ab initio molecular dynamics simulations. Despite the larger radius for Na^+ than Li^+, they found a much higher diffusivity for Na^+ in $Na_xAl_2O_3$ than for Li^+ in $Li_xAl_2O_3$ due to the weaker $Na-O$ bond strength than the $Li-O$ counterpart. These inspiring and interesting studies convey a vision that in the emerging field of SIBs, surface modification using Al_2O_3 coating could provide similar benefits as in the LIBs counterpart.

Herein we merge anatase TiO_2 nanostructuring and Al_2O_3 surface coating for the first time by a facile two-step method in order to improve the electrochemical performance of TiO_2 anode for SIBs. The electrochemical tests show that Al_2O_3 coating of TiO_2 improves the SIBs initial reversible capacity when an easy-to-prepare electrolyte formed by 1.0 M of $NaClO_4$ in PC is utilized, followed by a gradual capacity decay upon cycling. The influence of different electrolytes ($NaClO_4$ salt in various solvents) on cycling performance was then investigated for the modified sample in order to improve the cycling stability.

2. Experimental

2.1. Materials preparation

The two-step approach followed for the fabrication of Al_2O_3-modified TiO_2 (named as *m*-TiO_2 hereafter) nanoparticles starts from the synthesis of TiO_2 nanoparticles through hydrolysis of tetrabutyl titanate (TBT). Briefly, a solution containing 50 mL of ethanol and 0.1 mol of TBT was dropwise added into 10 mL of deionized water under magnetic stirring at room temperature. The obtained white precipitate was then dried at 110 °C for 6 h and subsequently calcined inside an oven at 400 °C for 5 h in air to obtain pure TiO_2 nanoparticles. In the second step, involving surface modification, 0.3 g of the as-prepared pure TiO_2 and 0.007 g of $Al(NO_3)_3\ 9H_2O$ (with Al:Ti molar percentage of 1%) were mixed in 20 mL of deionized water. The mixture solution was stirred under magnetic stirring for 2 h followed by ultrasonication for 0.5 h. Afterward, the mixture solution was thoroughly dried at 110 °C for 12 h and then calcined in an oven at 400 °C for 5 h in air to obtain the Al_2O_3-modified TiO_2 product.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku SmartLab X-ray powder diffractometer, equipped with a 9 kW CuKα rotating anode, operating at 40 kV and 150 mA. Transmission electron microscopy (TEM) images were obtained using a 200 kV microscope JEOL JEM-2200FS equipped with a Bruker Quantax 400 EDS system with an XFlash 5060 detector. High angle annular dark field (HAADF) scanning transmission electron microscope (STEM) examination and energy-dispersive X-ray spectroscopy (EDS) experiments were carried out on the same microscope. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Kratos Axis Ultra DLD spectrometer, using a monochromatic Al Kα source (15 kV, 20 mA).

2.3. Electrochemical tests

Type 2032 coin cells were assembled inside an Ar filled MBraun glovebox with moisture and oxygen levels maintained below 0.1 ppm. The working electrodes were prepared by mixing the active material (70 wt%), super P carbon (20 wt%), and polyvinylidene fluoride (PVDF, 10 wt%) in *N*-methylpyrrolidone (NMP). The resulting slurry was then casted onto a copper foil disk (Ø = 15 mm) and dried at 120 °C for 12 h in a vacuum glass oven. The loading amount of the active material on