



Full paper

Towards wearable electronic devices: A quasi-solid-state aqueous lithium-ion battery with outstanding stability, flexibility, safety and breathability

Zhuoxin Liu^a, Hongfei Li^a, Minshen Zhu^a, Yan Huang^b, Zijie Tang^a, Zengxia Pei^a, Zifeng Wang^a, Zhicong Shi^c, Jun Liu^c, Yang Huang^{d,*}, Chunyi Zhi^{a,e,**}

^a Department of Materials Science and Engineering, City University of Hong Kong, 83 Tat Chee Avenue, Hong Kong SAR, China

^b School of Materials Science and Engineering, Harbin Institute of Technology (Shenzhen), Shenzhen 518055, China

^c Guangdong Provincial Key Laboratory on Functional Soft Condensed Matter, School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, China

^d Shenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518000, China

^e Shenzhen Research Institute, City University of Hong Kong, Shenzhen 518000, China

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ABSTRACT

High-performance energy storage devices are in urgent need due to the fast development of wearable electronics, while the challenge of achieving outstanding flexibility has not been properly addressed yet, let alone the safety, another critical issue determines their practicability. Herein, we report a quasi-solid-state aqueous rechargeable lithium-ion battery (ARLIB) based on carbon cloth substrates and PVA-LiNO₃ gel polymer electrolyte (GPE). Thanks to the protective PPy coating layer on LiV₃O₈ and the use of solid GPE, the as-assembled ARLIB exhibits a good cycling stability of 98.7% and 79.8% capacity retention after 100 and 500 cycles, respectively. It also demonstrates exceptional flexibility to sustain various deformations including bending, squeezing, twisting and folding because of its solid-state design. Moreover, the ARLIB can be tailored into any desired shapes, and even be punched penetrative holes, exhibiting excellent safety. Thus, the creation of numerous tiny through-holes across the whole ARLIB body is testified feasible, and a designed breathability catering to the demand of comfortability in wearable devices is subsequently realized. Obviously, our study offers a promising strategy to construct flexible energy storage device with outstanding stability, flexibility, safety and breathability towards various wearable electronics.

1. Introduction

The blooming of portable consumer electronics in modern society have brought great convenience to daily life, for example, mobile phones empower us to deal with almost every business on the move, and we are thus bound to achieve more in fragmented time [1,2]. However, flexibility and wearability are still highly desired to ensure a convenient utilization of these portable electronics in different usage scenarios, which remain as a huge challenge to be properly addressed [3]. As an indispensable component, energy storage devices such as supercapacitors and batteries have been integrated into various kinds of electronic products. Nevertheless, these commercially available systems are intrinsically rigid because of their traditional stacking and packaging methods, which is a poor fit for portable features [4]. Numerous attempts have been made in recent years to develop flexible supercapacitors and great advances have been achieved [5–10]. Although

supercapacitors feature the advantages of high power density and long cycle life, they are still restricted to low energy density [11–14]. Whereas lithium-ion batteries (LIBs) have long been commercialized and are believed to be one of the most promising candidates to power future flexible and wearable electronics thanks to their high energy density. But most of the reported flexible LIBs are based on toxic and flammable organic electrolytes, suffering from the risks of causing fires and explosions, especially when they are being used under pressure and deformation, which makes it inappropriate for wearable electronics applications [15–17].

In 1994, a rechargeable LIB using an aqueous solution as electrolyte was first proposed by Dahn's group [18]. Following that, various kinds of aqueous rechargeable lithium-ion batteries (ARLIBs) have been developed [19–27], which are regarded as one of the most competitive energy storage systems because of their advantages of high safety, environmental friendliness and low cost, consequently making them an

* Corresponding author.

** Corresponding author at: Department of Materials Science and Engineering, City University of Hong Kong, 83 Tat Chee Avenue, Hong Kong SAR, China.
E-mail addresses: y.huang@outlook.com (Y. Huang), cy.zhi@cityu.edu.hk (C. Zhi).

ideal choice for wearable electronics. But due to the limitation of narrow electrochemical stable window of water (1.229 V), choice of active materials for both cathode and anode is substantially restricted [28,29]. Among several types of cathode materials suggested for ARLIBs, spinel LiMn_2O_4 (LMO) is the most promising one because of its simple synthesis, environmental friendliness, low cost and excellent rate capability, as reported in many literatures [30–33]. However, anode materials have long been the bottleneck of ARLIBs because of their poor stability in aqueous electrolyte, which is derived from the side reactions with water and/or oxygen, dissolution of active materials into aqueous solution, and structural change during charge/discharge cycles [34–36]. One method that has been proved effective is to coat active materials with another electronically conducting material or functionalized/conjugated polymer that can serve as a protecting layer since it is stable in aqueous solutions [37–42]. For example, Liu et al. [38,39] showed that the coating of polypyrrole (PPy) on $\alpha\text{-MoO}_3$ dramatically improved its cycling stability by preventing the dissolution of molybdenum ions. Similarly, Tang et al. [41,43] also showed that coating V_2O_5 /carbon nanotubes composite and MoO_3 with PPy improved the cycle performance of these materials as anodes in ARLIBs.

As a low-cost anode material, LiV_3O_8 (LVO) can be easily prepared at a relatively low temperature in air [44]. However, it has been obviated from the list of potential anode materials in aqueous electrolytes by many researchers in consideration of its extremely poor cycle performance [36]. In this study, we turn back to this material and successfully constructed a protective PPy layer both on the surface and between the space of LVO microrods. The conductive coating layer greatly enhanced the material's stability in aqueous electrolyte, and a flexible, wearable, quasi-solid-state ARLIB based on LVO anode and LMO cathode was subsequently designed and constructed by using soft carbon cloth substrates and PVA- LiNO_3 gel polymer electrolyte (GPE). Thanks to the protection of PPy coating layer and the use of solid GPE, which effectively suppressed the dissolution of LVO anode, improved the charge transfer resistance, and buffered the volume change during cycling, the ARLIB exhibited a greatly improved cycle performance, achieving a 94.0% capacity retention after 100 charge-discharge cycles at 0.3 A g^{-1} and a 79.8% capacity retention after 500 charge-discharge cycles at 0.5 A g^{-1} . In addition, it can be bent at various angles without evident capacity loss, and the demonstration of squeezing, twisting and folding testified its excellent flexibility. Due to the application of intrinsic soft and flexible carbon cloth and quasi-solid-state GPE, the ARLIB is highly tailorable and can even work well to power an electronic watch by using the separated half when it is bisected. To our knowledge, this is the first demonstration of tailorability reported for LIBs. Besides, punching penetrative holes didn't ruin our ARLIB, indicating its superior safety performance. Benefiting from both high flexibility and outstanding safety, we proposed a breathable ARLIB by achieving air permeability through punching hundreds of tiny through-holes across the device body, perfectly satisfying the need for comfort of wearable electronics. The features of good electrochemical performance, high flexibility, excellent safety and tunable air permeability make our ARLIB a promising candidate for a variety of wearable electronics.

2. Experimental section

2.1. Preparation of materials

Spinel LMO was synthesized by a solid-state method [22]. Specifically, 0.2100 g Li_2CO_3 (UNI-CHEM, AR) and 0.9412 g MnO_2 (Acros, 99%) were mixed evenly in an agate mortar with ethanol. After ethanol evaporation, the mixed powders were heated at $530 \text{ }^\circ\text{C}$ for 5 h in air, followed by calcination at $700 \text{ }^\circ\text{C}$ for 24 h in air. Then the obtained powders were slowly cooled down to room temperature. Similarly, a mixture of 0.1750 g Li_2CO_3 and 1.2307 g V_2O_5 (Alfa Aesar, 99.6%) were mixed evenly in an agate mortar with ethanol, and pristine LVO microrods were prepared by heating the dried mixture at $600 \text{ }^\circ\text{C}$ for

20 h in air with a slow cooling process to room temperature [44]. PPy coated LVO was prepared by an ethanol-assisted chemical polymerization method with FeCl_3 (Acros, 98%) as oxidant and SDBS (TCI, AR) as dopant [43]. Typically, 0.4 g pristine LVO was added into 20 mL 0.05 M SDBS aqueous solution and magnetically stirred for 30 min. Then 20 mL 0.2 M FeCl_3 solution was poured in and the resultant solution (solution 1) was kept stirring for 1 h under ice bath. 2–3 drops of pyrrole monomer were dissolved in 10 mL ethanol and thus formed the solution 2, which was subsequently added dropwise into solution 1 under ice bath, followed by continuous stirring for 1 h. After polymerization, a black material was collected by centrifugation and alternately washed with DI water and ethanol for at least 5 times before they were finally dried at $40 \text{ }^\circ\text{C}$ in a vacuum oven overnight.

2.2. Materials characterization

Structural and phase characterizations of the as-prepared materials were performed by a powder XRD using a Bruker D2 Phaser diffractometer with $\text{Cu K}\alpha$ irradiation ($\lambda = 1.54 \text{ \AA}$). The morphology of samples was characterized by an environmental scanning electron microscope (ESEM, FEI/Philips XL30) and a field emission transmission electron microscope (JEOL-2001). XPS analysis was conducted by an ESCALAB 250 photoelectron spectroscopy (Thermo Fisher Scientific) at 1.2×10^{-9} mbar using $\text{Al K}\alpha$ X-ray beam (1486.6 eV). The XPS spectra are charge corrected to the adventitious C 1s peak at 284.6 eV. Raman scattering spectra were obtained by a Raman spectroscopy (WITec alpha300 access) with a laser of 532 nm wavelength and a grating of 600 g mm^{-1} .

2.3. Electrodes preparation and cell assembly

Prior to be used, the carbon cloth underwent an acid-treatment to improve its wettability, which refers to a two-hour ultrasonication in mixed 69% HNO_3 (VWR Chemicals) and 96% H_2SO_4 (VWR Chemicals) acid (3:1, volume ratio). After ultrasonication, the acid-treated carbon cloth was washed with DI water and oven-dried at $80 \text{ }^\circ\text{C}$ overnight. The as-prepared LMO and LVO powders were directly used as active materials without any further treatment. Generally, a mixture of active material (LMO or LVO), conducting additive (acetylene black, AB) and binder (polytetrafluoroethylene, PTFE) with a mass ratio of 80:10:10 was finely ground in an agate mortar with the assistance of isopropanol to form a slurry. The slurry was subsequently coated thoroughly onto carbon cloth current collectors with a blade, followed by oven-drying at $80 \text{ }^\circ\text{C}$ overnight. The mass loading of active materials on carbon cloth was controlled in the range of $2\text{--}10 \text{ mg cm}^{-2}$, and the mass ratio of LMO to LVO was set to be around 1:2.2 in order to balance the capacities of cathode and anode. The gel polymer electrolyte was prepared by dissolving 6.0 g PVA powder (UNI-CHEM, LR, 100,000 M W.) into 60 mL 5 M LiNO_3 solution at $90 \text{ }^\circ\text{C}$ under stirring. Prior to assembling, the cellulose paper serving as a separator was immersed in PVA- LiNO_3 solution for 15 min and then sandwiched between two electrodes. The obtained full cell was kept at room temperature for 2 h to allow electrolyte to wet the electrodes.

2.4. Electrochemical test

Electrochemical performances of LMO and LVO electrodes in 5 M LiNO_3 aqueous solution were investigated with a three-electrode system using a Pt sheet and a saturated calomel electrode (SCE, 0.242 V vs. NHE) as counter and reference electrodes, respectively. Electrochemical performances of full ARLIBs were performed in CR2032-type coin cells. Cyclic voltammetry curves and electrochemical impedance spectroscopy (100 kHz to 0.01 Hz) were obtained by an electrochemical workstation (CHI 760D). Galvanostatic charge/discharge measurements were conducted by a Land 2001A battery testing system. The oxygen in electrolyte was not eliminated for all tests.

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