Journal of Power Sources 274 (2015) 280–285

Contents lists available at ScienceDirect

Journal of Power Sources

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

Preferential orientation of I_2-LiI(HPN)$_2$ film for a flexible all-solid-state rechargeable lithium–iodine paper battery

Fang-Chao Liu [a], Zulipiya Shadike [a], Fei Ding [b], Lin Sang [b], Zheng-Wen Fu [a,*]

[a] Shanghai Key Laboratory of Molecular Catalysts and Innovative Materials, Department of Chemistry & Laser Chemistry Institute, Fudan University, Shanghai 200433, PR China

[b] National Key Laboratory of Science and Technology on Power Sources, Tianjin Institute of Power Sources, Tianjin 300384, PR China

HIGHLIGHTS

- We have found a highly preferential orientation of I_2-LiI(HPN)$_2$ film on the paper.
- We have fabricated a new all-solid-state Li/I_2-LiI(HPN)$_2$ film paper battery.
- We have examined the electrochemical behaviors of Li/I_2-LiI(HPN)$_2$ film paper battery at high temperatures of 70 °C.

ARTICLE INFO

Article history:
Received 31 July 2014
Received in revised form
7 October 2014
Accepted 9 October 2014
Available online 16 October 2014

Keywords:
All-solid-state battery
Lithium–iodine
Film
Preferred orientation

ABSTRACT

A highly preferred orientation of I_2-LiI(HPN)$_2$ film on the paper was found. The electrochemical property of a new flexible all-solid-state Li/I_2-LiI(HPN)$_2$ film paper battery was examined at wide temperatures for the first time. This paper battery is capable of achieving a high discharge energy of 250 Wh/kg with a plateau potential region at 2.70 V versus Li/Li$^+$ at 70 °C. The interfacial layer of (LiI)$_{(1+x)}$I$_{(2-x)}$ (HPN)$_2$ instead of LiI between lithium and I_2-LiI(HPN)$_2$ film should be responsible for the high electrochemical activity of the lithium–iodine paper battery.

1. Introduction

The growing demand of electric vehicles (EV) and hybrid electric vehicles (HEV) has intensified the research and development of lithium ion batteries. An extensive research effort is currently underway to develop solid state rechargeable lithium batteries based on inorganic solid state electrolyte for the application of the EV or HEV, because they have an extreme safety and reliability to avoid the combustibility of nonaqueous electrolytes, and to resist to shock and vibration and to resist to pressure and temperature variations [1,2]. Previously most solid state batteries were reported in the form of thin film for applications in micro- and nano-scopic devices as miniaturized power sources due to the low ionic conductivities of these inorganic electrolytes such as lithium phosphorus oxynitride (LiPON) [3,4]. For example, the primary all-solid-state lithium/iodine battery power for the cardiac pacemaker. A monomolecular layer of crystalline lithium iodine formed between a lithium anode and an iodine–complex cathode could serve as a Li$^+$ conductor with the pass of lithium ions but not iodine molecular or ions [5,6]. Recently, some sulfide-based electrolytes with high ionic conductivities can potentially ensure a high energy densities of all-solid-state batteries comparable to those of lithium ion batteries using liquid electrolytes [7–10]. We reported a solid state lithium iodine battery with a complex cathode film of iodine and LiI(3-hydroxypropionitrile)$_2$ (chemical formula: LiI(C_3H_5NO)$_2$, abbreviation: LiI(HPN)$_2$) as cathode, and with a I$^-$ ionic conductor of LiI(HPN)$_2$ as solid electrolyte [11]. However, these solid state rechargeable lithium batteries still suffer from low power density and the high cost for their large-scale fabrications. Much work have been conducted to address the issues existed in lithium–iodine battery for improving its performance by lowering the internal resistance [12–15]. Here, a highly preferential orientation of I_2-LiI(HPN)$_2$ film grown on the paper as an iodine

* Corresponding author. Tel.: +86 21 65642522; fax: +86 21 65102777.
E-mail address: zwfu@fudan.edu.cn (Z.-W. Fu).

http://dx.doi.org/10.1016/j.jpowsour.2014.10.057
0378-7753/

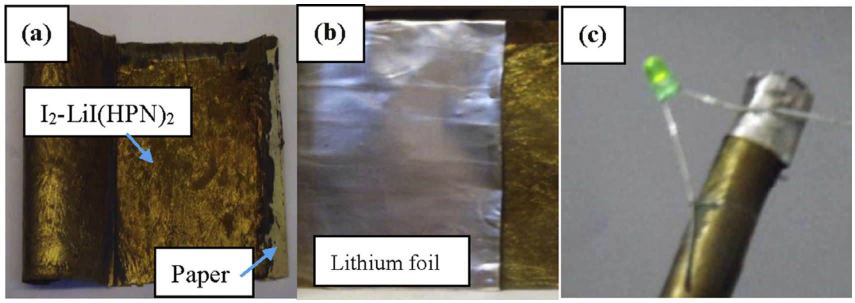

Fig. 1. The digital picture of (a) a golden luster I_2-LiI(HPN)$_2$ film on the paper; (b) the assembled Li/I_2-LiI(HPN)$_2$ film paper battery by simply pressing one Li-foil onto I_2-LiI(HPN)$_2$ film paper with a suitable mass; (c) a bendable Li/I_2-LiI(HPN)$_2$ film battery turning on a blue LED in bent condition. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

cathode is reported for the first time. A new all-solid-state Li/I_2-LiI(HPN)$_2$ film paper battery can be constructed by simply coating an I_2-LiI(HPN)$_2$ film paper on the surface of lithium plate, in which a new self-healing separator layer of $(LiI)_{(1+x)}I_{(2-x)}$(HPN)$_2$ is formed gradually and spontaneously by the chemical reaction of Li and I_2-LiI(HPN)$_2$ when they contact with each other closely. This cell fabrication is utterly different from previous solid state lithium iodine batteries by coating thin solid LiI(HPN)$_2$ electrolyte layer on the surface of a Li plate and then exposing its surface to I_2 vapor to form Li/LiI(HPN)$_2$/I_2-LiI(HPN)$_2$ cell [11]. The electrochemical properties of Li–I_2 paper battery will be examined at wide temperatures, and its high electrochemical activity will be discussed. Our results have demonstrated that the highly preferential orientation of I_2-LiI(HPN)$_2$ film paper should play an important in the improved electrochemical activity of lithium iodine battery.

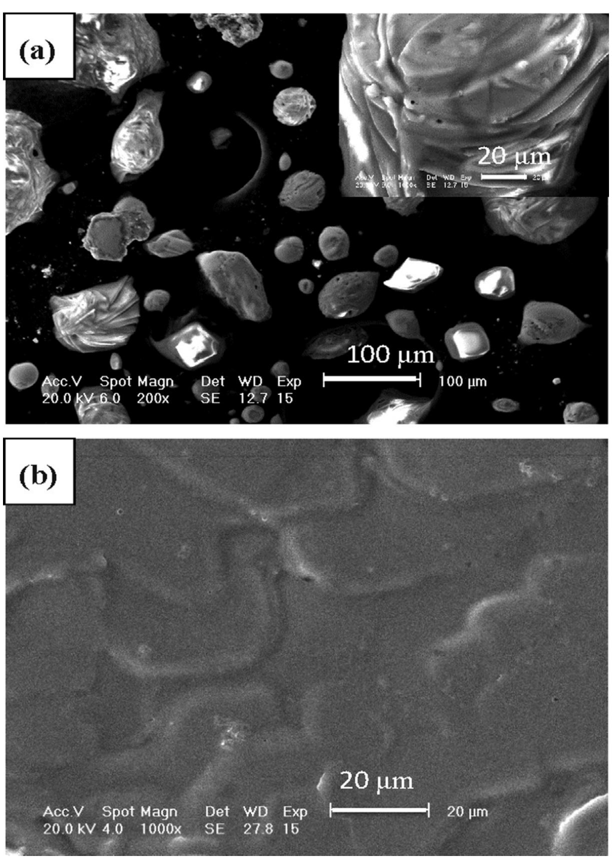

Fig. 2. Scanning electron microscopic images of (a) I_2-LiI(HPN)$_2$ powder with magnification of 200× and 1000× (inset) and (b) I_2-LiI(HPN)$_2$ film on the paper with magnification of 1000×.

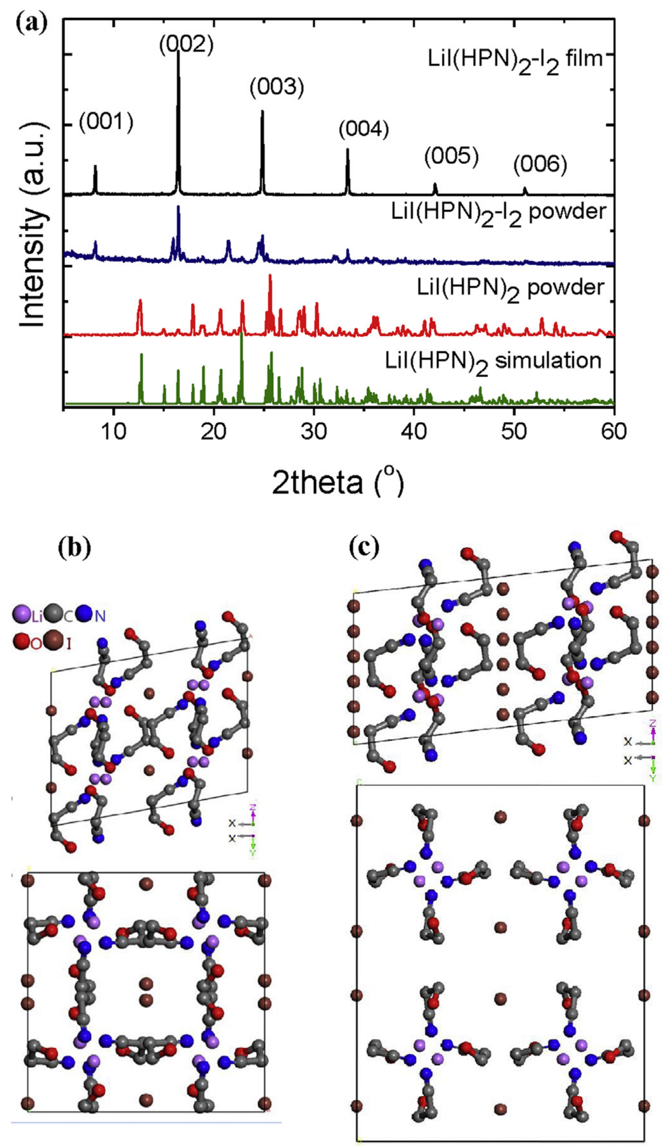

Fig. 3. (a) XRD patterns of LiI(HPN)$_2$ simulation, LiI(HPN)$_2$ powder, I_2-LiI(HPN)$_2$ powder and I_2-LiI(HPN)$_2$ film; (b) the structure of LiI(HPN)$_2$ and (c) possible structure of I_2-LiI(HPN)$_2$ (both observed from c and b axis).