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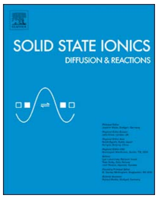

A super-long life rechargeable aluminum battery

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ABSTRACT

High energy and power density rechargeable batteries with low cost, long cycle life and high safety remain a great demand of portable electronics and grid storage systems. Recently, rechargeable aluminum batteries (RABs) have attracted much attention owing to its high volumetric capacity (8046 mAh cm^{-3}), low cost and ultra-safety. However, harsh reaction conditions and complicated processes are usually used in preparation of electrode materials, hindering the practical application. Herein, a commercial ordered mesoporous carbon (CMK-3) as a cathode for RABs is proposed, which shows a super-long life of > 36,000 charge/discharge cycles with a high coulombic efficiency of > 97% and excellent rate performance up to 3000 mA g^{-1}. Moreover, The Al/CMK-3 battery has a high energy density of ~45 Wh kg^{-1}. Last, the structure changes and (de)intercalation of chloroaluminate anions into the mesopores of CMK-3 during the charge/discharge process were checked by *ex-situ* scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), Raman and X-ray photo spectroscopy (XPS). Commercially availability and affordable cost of the cathode material make Al/CMK-3 battery more promising for wearable and portable appliances.

1. Introduction

Sustainable and environmentally friendly energy storage and conversion systems have attracted intense attention, especially electrochemical batteries. Li metal-based rechargeable batteries offer high capacity and energy density but high cost and low safety [1–4]. Therefore, in the past decade, the research focus has shifted abruptly towards the quest of post-lithium based rechargeable batteries [5–10]. Therein, rechargeable aluminum batteries (RABs) have demonstrated potential applications in the near future due to its ultrahigh volumetric capacity (8046 mAh cm^{-3}), low cost and very high safety without any fire risks [11–13].

Recently, a wide range of cathode materials have been reported for RABs, for instance, metal oxides, sulfides, chlorides, carbon-based, and many others [14–36]. Nevertheless, the research of cathodes for RABs has elucidated that the carbon-based materials are of great significance for the stable, long life and high operating voltage RABs [21,28,30,35,37–39]. However, the reported carbon-based cathode materials involve complex and high-cost synthesis processes, which are hard to commercialize [21,28,30,38,40]. As a typical example, the defect-free graphene which exhibits very long cycle life in RABs was synthesized at a high temperature of 3000 °C [38]. Accordingly, the carbon-based materials which are inexpensive or already commercially available would be expected as practical cathode materials without compromising electrochemical performance of RABs and can bring RABs from lab scale to large production lines.

Owing to its high surface areas (1000–2000 m^2 g^{-1}) and pore volumes (0.5–1 cm^3 g^{-1}) as well as excellent conductivity, [41–43] the ordered mesoporous carbon, CMK-3 has been widely explored in the fields of catalysis, pollutant absorbents, hydrogen storage, supercapacitors and batteries [42,44–48]. Importantly, it is already commercially available with affordable costs. In this communication, CMK-3 is reported for the first time as a cathode material for RABs. The resultant Al/CMK-3 battery shows > 36,000 reversible cycles at a current density of 980 mA g^{-1} (15C, where 1C = ~60 mAh g^{-1} [37]), > 97% coulombic efficiency and ~45 Wh kg^{-1} energy density. The intercalation/deintercalation of chloroaluminate anions into CMK-3 during the charge/discharge process was confirmed by *ex situ* scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), Raman and X-ray photoelectron spectroscopy

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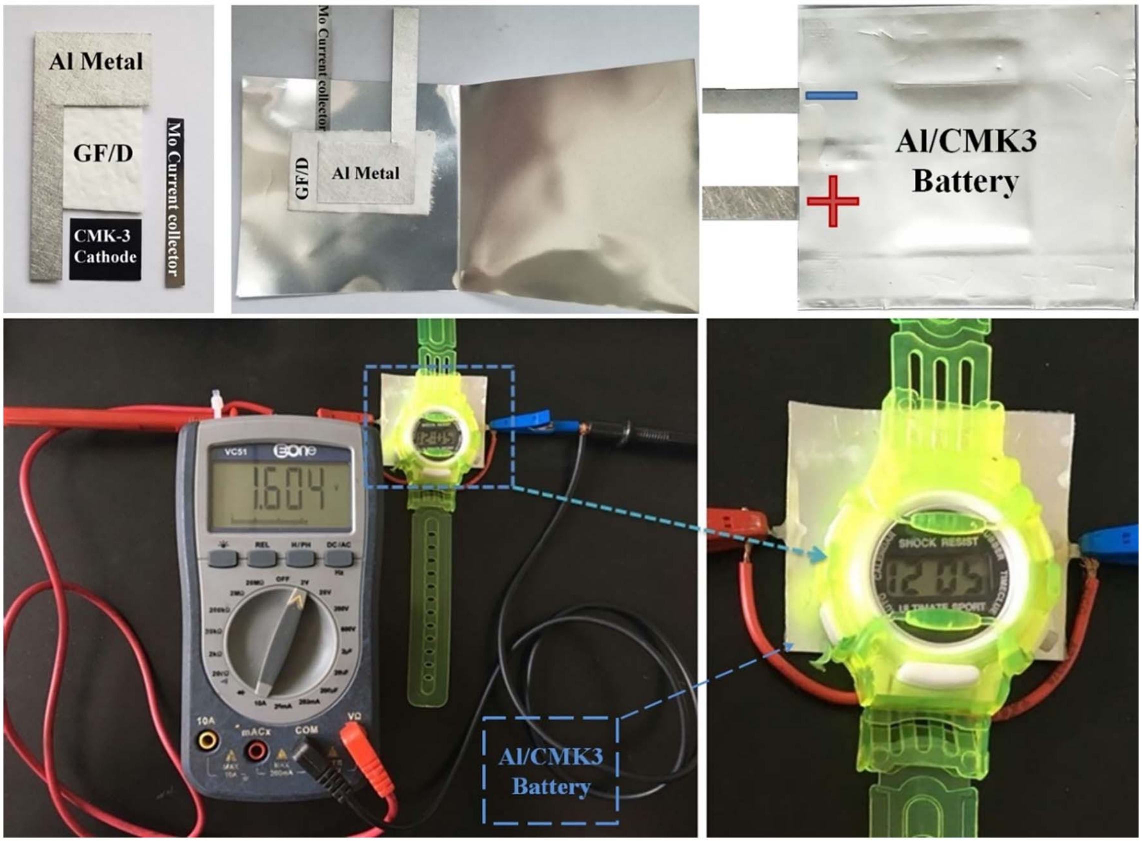

Fig. 1. Demonstration of the Al/CMK-3 pouch cell fabrication (top), and the practical application of the battery in digital wristwatch (bottom).

(XPS). This work not only reports a low cost and commercial cathode material but paves an avenue for the commercialization of RABs.

2. Experimental

2.1. Preparation of CMK-3 electrode

In order to obtain uniform slurry for the fabrication of cathode film, CMK-3 was mixed with PTFE binder dissolved in NMP disperser (25 mg ml^{-1}). Additionally, Super-P was also added to enhance overall conductivity of the cathode. All cathode components, CMK-3, Super-P and PTFE dissolved in NMP were added in the ratio of 7:2:1 and mixed in a mortar and pestle to get homogenous slurry. The as-obtained slurry was pasted on molybdenum (Mo) current collector by using a doctor blade with a film thickness of 150 µm. Later, the slurry was dried in an oven at 60 °C for overnight before cutting into rectangular shaped (1.5 mm × 1.0 mm) cathodes for the fabrication of pouch cells.

2.2. Preparation of [EMIm]AlxCly IL electrolytes

A room temperature IL electrolyte was prepared by mixing 1-ethyl-3methyl-imaidazolium chloride [EMIm]Cl (TCI-Japan, 97%) and anhydrous $AlCl_3$ (Sigma-Aldrich, 99.999%). The room temperature [EMIm]Al_xCl_y IL electrolyte was prepared in a glove box under an Argon atmosphere (H_2O and $O_2 < 0.01$ ppm) as both components of electrolyte are highly hygroscopic. $AlCl_3$ and [EMIm]Cl were mixed together with a molar ratio of 1.3. Finally, the resulting light-yellow transparent liquid was stirred at room temperature for 10–20 min.

2.3. Fabrication of Al/CMK-3 pouch cells

The pouch cells were fabricated in a glovebox (H_2O and $O_2 < 0.01$ ppm) to avoid any contact with moisture or air. The as-prepared CMK-3 cathode (1.5 mm × 1.0 mm) was utilized against the ultrapure Al foil (0.2 mm, 99.9999%, Alfa-Aesar) anode which was separated by a single layer of microglass fiber filter (GF/D) separators (Fig. 1, top). After the injection of IL electrolyte, all of the battery components were sealed inside aluminum laminate sheet (C80-400) by utilizing an impulse heating sealer machine (Bleuets FR-300B).

2.4. Characterizations

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500/PC diffractometer employing Cu Kα radiation (λ = 1.5418 Å) operating at 50 kV and 200 mA. The Brunauer-Emmett-Teller (BET) surface area and pore structure were measured by N_2 adsorption/desorption using a Micromeritics 2020 M instrument. Before exposure to N_2, the sample was outgassed at 300 °C for 5 h. Field-emission scanning electron microscopy (FESEM) was performed on a Hitachi SU-70 microscope. High resolution transmission electron microscopy (HRTEM) was conducted on a JEOL JEM-2010 microscope at an accelerating voltage of 200 kV. XPS data were obtained on an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charging effects, the binding energies were calibrated using the C1s hydrocarbon peak at 284.80 eV.

2.5. Electrochemical performance measurements

The galvanostatic charge/discharge, cycle life and rate capability tests were performed at a LAND (Wuhan) charge/discharge apparatus at constant charging and discharging current densities in the voltage range of 0.5 to 2.3 V at 25 ± 1 °C. The electrochemical impedance spectroscopy (EIS) measurements were conducted on SP-300 at a frequency range of 100 kHz to 100 mHz.