



Exploration of cobalt phosphate as a potential catalyst for rechargeable aqueous sodium-air battery



Baskar Senthilkumar ^a, Ziyauddin Khan ^a, Sangmin Park ^a, Inseok Seo ^{b, **}, Hyunhyub Ko ^a, Youngsik Kim ^{a, *}

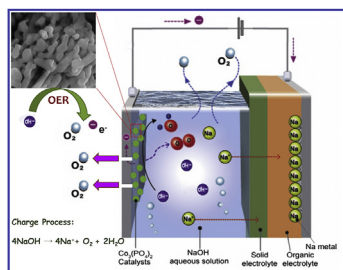
^a School of Energy & Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), UNIST-gil 50, Ulsan, 689-798, Republic of Korea

^b Research Institute of Industrial Science and Technology, POSCO Global R&D Center, 180-1 Songdo-Dong Yeonsu-Gu, Incheon, 406-840, Republic of Korea

HIGHLIGHTS

- $\text{Co}_3(\text{PO}_4)_2$ nanomaterial was synthesized by facile precipitation technique.
- Bi-functional electrocatalytic activity of nano- $\text{Co}_3(\text{PO}_4)_2$ was demonstrated.
- The energy efficiency of Na-air cell was attained up to 83% by $\text{Co}_3(\text{PO}_4)_2$ catalyst.
- The Na-air cells were yielded low overpotential and good cycling stability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 4 January 2016

Received in revised form

1 February 2016

Accepted 6 February 2016

Available online 16 February 2016

Keywords:

Cobalt phosphate

Electrocatalyst

Sodium-air battery

Aqueous electrolyte

Sodium super ionic conductor

ABSTRACT

Bifunctional catalysts are prominent to attain high capacity, maximum energy efficiency and long cycle-life for aqueous rechargeable Na-air batteries. In this work, we report the synthesis of bi-functional noble metal free, $\text{Co}_3(\text{PO}_4)_2$ nanostructures by facile precipitation technique and evaluated its electrocatalytic activity. $\text{Co}_3(\text{PO}_4)_2$ nanostructure was investigated as a potential electrocatalyst for rechargeable aqueous Na-air battery for the first time. The synthesized $\text{Co}_3(\text{PO}_4)_2$ grain-like nanostructures showed better oxygen evolution activity compared to Pt/C catalyst. The fabricated Na-air battery with the $\text{Co}_3(\text{PO}_4)_2$ catalyst as air-cathode delivered low overpotential and its round trip energy efficiency reached up to 83%. The Na-air battery exhibited stable cycle performance up to 50 cycles.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Due to high energy densities, rechargeable metal air batteries have been emerged as promising candidate for future energy technologies [1–3]. Lithium air batteries have been captivated

scientific community attention owing to its high theoretical energy density (5200 Wh kg^{-1}) but low Li abundance, poor cyclic stability and high overpotential makes lithium air batteries expensive and unpractical [4–6]. In recent times, sodium air batteries (referred as Na-air) have gained much attention as an alternate to lithium air batteries due to its safety, cost and higher ionic conductivity in aqueous, non-aqueous and solid electrolyte [6,7]. However, non-aqueous Na-air batteries have been studied much but less efforts have been given to aqueous Na-air batteries. Though non-aqueous

* Corresponding author.

** Corresponding author.

E-mail addresses: isseo@rist.re.kr (I. Seo), ykim@unist.ac.kr (Y. Kim).

Na-air battery have disadvantage due to the formation of solid and insoluble discharge product and blockage of air electrode pores by solid discharge product which eventually reduces the performance of battery. Furthermore, aqueous Na-air batteries have ultimate advantage due to the formation of highly water soluble discharge product (sodium hydroxide) which increases the performance of the cell having low overpotential, high round trip efficiency and good cyclic stability [7,8]. Despite these advantages, aqueous Na-air battery research has not been intensified and till date only few research articles have been published in which noble metal catalysts were used as air electrode [8–11]. However, rechargeability of aqueous Na-air batteries was demonstrated recently using Pt and nanoporous gold air electrodes [10,11]. But, cycling stability and efficiency was tested only up to 18 cycles. Improving efficiency and cycling stability of aqueous Na-air cells are still challenging, moreover, till date transition metal oxides have not been utilized as air electrode for rechargeable aqueous Na-air batteries.

A rechargeable metal-air battery can be designed by the proper selection and fabrication of air electrode which is commonly known as bifunctional electrocatalyst [12,13]. The bifunctional electrocatalyst reduces oxygen via oxygen reduction reaction (ORR) during discharge of battery, while at charge; oxygen is evolved via oxygen evolution reaction (OER) at high applied voltage. Herein, we have prepared noble metal free $\text{Co}_3(\text{PO}_4)_2$ by facile and cost-effective precipitation method followed by its electrochemical characterization and fabrication of an aqueous Na-air battery using $\text{Co}_3(\text{PO}_4)_2$ as an electrocatalyst for the first time. Scheme 1 represents the schematic illustration of our designed aqueous Na-air battery with $\text{Co}_3(\text{PO}_4)_2$ as an air cathode. Our motivation of this work is to utilize noble metal free air electrode and investigate the rechargeability of aqueous Na-air battery. The fabricated cell display low overpotential (0.59 V), 83% round trip efficiency and good cyclic stability which is superior to the current lithium air batteries and recent reports on aqueous Na-air batteries [4,10,11].

2. Experimental section

2.1. Synthesis of cobalt phosphate

Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), sodium hydroxide pellets (NaOH) and cobalt phosphate octahydrate $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ were purchased

from Sigma Aldrich and used as received. For the synthesis of $\text{Co}_3(\text{PO}_4)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (4.37 g) and $\text{NH}_4\text{H}_2\text{PO}_4$ (1.70 g) were dissolved in distilled water followed by the addition of 1 M NaOH aqueous solution and pH was adjusted to 7. The resulting solution was stirred magnetically up to 5 h. Thereafter, the precipitate was collected and washed well with distilled water. The collected sample was dried at 80 °C overnight. The obtained powder was calcined at 700 °C for 5 h in muffle furnace to get pure phase of cobalt phosphate. The heating rate was fixed at 2 °C min^{-1} while cooling was done naturally.

2.2. Preparation of electrodes and configuration of aqueous Na-air battery

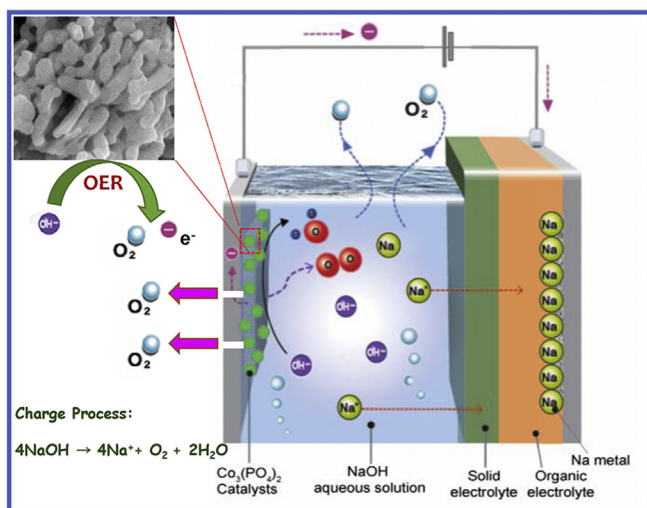
For air electrode preparation, a slurry mixed with cobalt phosphate, conductive carbon black Super-P (TIMCAL), polyvinylidene fluoride (PVDF, Sigma Aldrich) at the ratio of 80:10:10 weight percent was coated on the 2 × 2 cm carbon paper and kept it for drying at 80 °C. The weight of active air electrode material was 12 mg. The anode part of battery was assembled as pouch cell in glove box which have Ar atmosphere and less than 1 ppm water. Na metal, as anode, was attached on Nickel mesh (Woolf metal Corporation) followed by dropping 1 M NaCF_3SO_3 (Sigma Aldrich) in tetra ethylene glycol dimethyl ether (TEGDME, Sigma Aldrich) solution as organic electrolyte on metallic sodium. This anode part was attached and sealed with solid electrolyte NASICON ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$) whose one side was kept exposed to air. Solid electrolyte NASICON was prepared by solid state route [14]. $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, SiO_2 and ZrO_2 were mixed and then calcined at 400 and 1100 °C. After being mixed and calcined again, the powder was pressed into a pellet, which was sintered at 1230 °C. The NASICON ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$) pellet was ground with emery paper to achieve thickness (0.8 mm) and area (2 cm^2 , diameter of 8 mm). The anode compartment and air electrode compartment was attached with NASICON separator. 0.1 M NaOH solution was used as aqueous electrolyte. Configuration of assembled cell consisted of (–) Ni mesh|metallic Na|organic electrolyte|NASICON|0.1 M NaOH| $\text{Co}_3(\text{PO}_4)_2$ |Ti mesh (+).

2.3. Characterization

The powder X-ray diffraction (XRD) data was collected using the Bruker D8 Advanced diffractometer equipped with Cu-K α radiation and a diffractometer monochromator that was operated at 40 kV and 40 mA. The morphology of the $\text{Co}_3(\text{PO}_4)_2$ nanostructures were analyzed by scanning electron microscopy (SEM), and the particles were further characterized using transmission electron microscopy (TEM). The TEM microscope was an aberration-corrected JEOL JEM-2100F operated at 200 kV. Samples were made suitable for TEM observation by dispersing the material into ethanol and dropping them onto lacy-carbon coated copper TEM grids. The chemical bonding was investigated by X-ray photoelectron spectrometry (XPS, K-alpha, Thermo Fisher, UK). The electrocatalytic activity of the $\text{Co}_3(\text{PO}_4)_2$ and Pt/C catalysts was investigated using a rotating ring-disk electrode (RRDE) in an O_2 -saturated 0.1 M NaOH with IviumStat. The electron transfer number (n) was calculated by the following equation [3]

$$n = 4 \frac{I_d}{I_d + I_r/N}$$

where I_d is the disk current, I_r is the ring current, and N is the current collection efficiency of the Pt ring, which was determined to be 0.41. Electrochemical performance tests were carried out using an automatic galvanostatic charge-discharge unit, WBCS



Scheme 1. Schematic representation of rechargeable aqueous Na-air battery with $\text{Co}_3(\text{PO}_4)_2$ as air cathode in charge state.

Download English Version:

<https://daneshyari.com/en/article/1283712>

Download Persian Version:

<https://daneshyari.com/article/1283712>

[Daneshyari.com](https://daneshyari.com)