Journal of Power Sources 307 (2016) 208–213

Contents lists available at ScienceDirect

Journal of Power Sources

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

Short communication

Bipolarly stacked electrolyser for energy and space efficient fabrication of supercapacitor electrodes

Xiaojuan Liu [a], Tao Wu [a], Zengxin Dai [b], Keran Tao [a], Yong Shi [c], Chuang Peng [a, b, *], Xiaohang Zhou [d], George Z. Chen [a, d, **]

[a] *Department of Chemical and Environmental Engineering, Faculty of Science and Engineering, University of Nottingham Ningbo Campus, Ningbo, 315100, China*

[b] *College of Materials Science and Engineering, Hunan University, Changsha, Hunan, 410082, China*

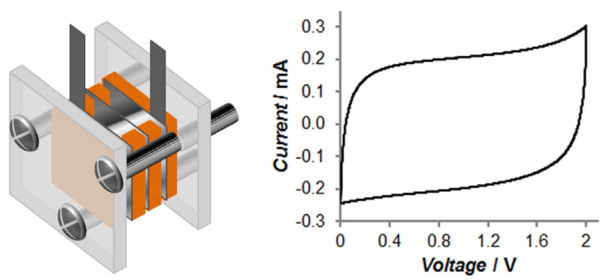
[c] *Department of Mechanical, Materials and Manufacturing Engineering, Faculty of Science and Engineering, University of Nottingham Ningbo Campus, Ningbo, 15100, China*

[d] *Department of Chemical and Environmental Engineering, Energy and Sustainability Research Division, Faculty of Engineering, University of Nottingham, University Park, Nottingham, NG7 2RD, UK*

HIGHLIGHTS

- Half electrolysis is verified in bipolarly stacked electrolyser for the first time.
- Conducting polymer electrodes are prepared at high energy and current efficiency.
- The electrodes exhibit excellent supercapacitor behaviours.
- The electrolyser offers a facile route for making compact supercapacitor stacks.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 November 2015
Accepted 1 January 2016
Available online xxx

Keywords:
Electrode fabrication
Supercapacitor
Stacked bipolar electrolyser
Electrodeposition
Conducting polymer
Half electrolysis

ABSTRACT

Stacked electrolysers with titanium bipolar plates are constructed for electrodeposition of polypyrrole electrodes for supercapacitors. The cathode side of the bipolar Ti plates are pre-coated with activated carbon. In this new design, half electrolysis occurs which significantly lowers the deposition voltage. The deposited electrodes are tested in a symmetrical unit cell supercapacitor and an asymmetrical supercapacitor stack. Both devices show excellent energy storage performances and the capacitance values are very close to the design value, suggesting a very high current efficiency during the electrodeposition. The electrolyser stack offers multi-fold benefits for preparation of conducting polymer electrodes, i.e. low energy consumption, facile control of the electrode capacitance and simultaneous preparation of a number of identical electrodes. Therefore, the stacked bipolar electrolyser is a technology advance that

* Corresponding author. Department of Chemical and Environmental Engineering, Faculty of Science and Engineering, University of Nottingham Ningbo Campus, Ningbo, 315100, China.

** Corresponding author. Department of Chemical and Environmental Engineering, Faculty of Science and Engineering, University of Nottingham Ningbo Campus, Ningbo, 315100, China.

E-mail addresses: Chuang.peng@nottingham.edu.cn (C. Peng), George.chen@nottingham.ac.uk (G.Z. Chen).

http://dx.doi.org/10.1016/j.jpowsour.2016.01.006

offers an engineering solution for mass production of electrodeposited conducting polymer electrodes for supercapacitors.

1. Introduction

Conducting polymers, such as polyaniline (PAN), polypyrrole (PPY) and poly [3, 4-ethylenedioxythiophene] (PEDOT), possess high electronic conductivity and redox activity at their doped states, leading to pseudocapacitive behaviours [1–3]. The electric charge is stored within the polymer chain so the specific capacitance is notably higher than porous carbonaceous materials, in which the charge is stored superficially at the double layer. Compared to transition metal oxides which also have a high specific pseudocapacitance, conducting polymers are superior in term of electronic conductivity. As a result, to exhibit supercapacitor behaviour, transition metal oxides have to be made into very thin coatings (normally within the range of a few nanometres and a few micrometres) on a current collector, while for conducting polymers, thick films over a few millimetres have demonstrated excellent capacitive behaviour [4]. Other advantages of conducting polymers include easy processing and ability to form composites with other materials including carbon nanotubes and graphene [4–8]. The applications of conducting polymers and their composites in supercapacitor electrodes have been extensively investigated [6–10].

Compared to other methods for fabrication of conducting polymer electrodes, electrochemical polymerisation or electrodeposition has demonstrated multiple benefits such as one-step template-free preparation [2,4,10], facile control of electrode capacitance by deposition charge [4], consistent electrochemical performance [4], excellent conductivity [3,9], binder-free electrodes [4,9,10], precise control of the oxidation or doping level [11]. However, most of the current researches only focus on the three-electrode method to perform potentiostatic, galvanostatic or potentiodynamic deposition assisted by a reference electrode, while little has been reported on commercial type two-electrode reactor/electrolyser for electrodeposition of conducting polymers. The results obtained from the three-electrode studies only provide theoretical basis for electrode production by electrodeposition at lab scale. A few technical concerns need to be resolved in order to further test the feasibility of industrial scale production of electrodeposited electrodes. Firstly a single cell electrolyser only produces one electrode at one time. A stacked electrolyser with bipolar plates may solve this problem because the cell is capable of simultaneously preparing a number of identical electrodes, i.e., electrodes with the same deposition charge and hence the same electrode capacitance. To the best of our knowledge, electrodeposition of conducting polymers in a bipolarly stacked electrolyser has never been reported in literature. Secondly, the electrolysis voltage and current efficiency during electrodeposition in single or stacked electrolyser are of high importance because they determine the energy consumption and yield of the electrodeposition process. Another important concern is the selection of electrode substrate material particularly when the deposition is carried out in aqueous solutions. In laboratory researches, noble metals such as Pt and carbon based materials such as glassy carbon or graphite are commonly used as a chemically stable and electrically conducting substrate [4,5]. However, in industrial processes, the former is too expensive and the latter has poor mechanical properties and is thus difficult to make thin and robust sheet. Titanium (Ti) is a light weight metal with strong mechanical properties. Moreover, unlike other commercial metals such as steel or nickel, Ti is very stable in aqueous solution even at high electrode potentials owing to the protection of a thin semiconducting surface oxide layer. The price of commercial Ti is expected to be significantly reduced with the development of newly emerged technologies such as direct reduction of TiO_2 in molten salts [12].

To clear the above obstacles to industrial manufacturing of electrodeposited conducting polymer electrodes, this paper reports the design and construction of a new bipolarly stacked electrolyser for galvanostatic electrodeposition of polypyrrole (PPY) for both symmetrical and asymmetrical supercapacitor electrodes. The electrolyser is capable of simultaneously producing a large number of electrodes with identical capacitance. An important and unique feature of the electrolyser is that the cathode side of the bipolar plate is coated with activated carbon (Cabot Monarch 1300 pigment black or CMPB). This novel design adopts and extends the newly proposed concept of half electrolysis [13] during the electrodeposition, which reduces the applied voltage on every cell in the stack and hence offers multiple savings in the energy consumption. The design is also beneficial for making compact supercapacitor stacks afterwards because the as-prepared bipolar electrodes are coated with CMPB and conducting polymer on the two sides of the Ti sheet, i.e., the negative and positive electrode respectively. The capacitance of the electrodes can be easily controlled by the deposition charge and CMPB loading. Therefore the bipolarly stacked electrolyser ensures individual electrodes have the same capacitance value and this feature is of high technical importance from the viewpoint of process engineering for design and construction of bipolarly stacked supercapacitors.

2. Material and methods

2.1. Design of the stacked bipolar electrolyser

Square Ti sheets (2 × 2 cm, thickness 0.1 mm) coated with or without CMPB were employed as both the end and bipolar electrodes. Pt foil with the same size was used for control experiment. Rubber U housings were placed between electrodes to form individual compartments/electrolysers. Before electrodeposition, electrolyte with pyrrole monomers was injected into the rubber framed individual compartments using a syringe or a fine tip transfer pipette. As shown in Fig. 1, a typical two-compartment stacked electrolyser was assembled with two rubber pads, three Ti sheets, two rubber U housings and two acrylic perspex supporting plates. The Ti sheet in the middle serves as a bipolar electrode. The U housing had a wall thickness of 0.4 cm, so the effective electrode area for electrodeposition is $(2-0.4 \times 2)^2 = 1.44\ cm^2$. The two supporting plates were joined by means of three stainless steel screws which tighten the whole reactor and ensure each individual compartment does not leak.

2.2. Electrochemical deposition and characterisation

A PGSTAT100 Autolab potentiostat or CHI760D potentiostat was used for all electrochemical control and measurements, i.e., cyclic voltammetry (CV), galvanostatic deposition and galvanostatic