Journal of Power Sources xxx (2013) 1–9

Contents lists available at ScienceDirect

Journal of Power Sources

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

Carbon nanotube-assisted electrodeposition. Part I: Battery performance of manganese oxide films electrodeposited at low current densities

Ali Eftekhari*, Foroogh Molaei

National Institute of Arts & Sciences, 411 Walnut Street, Green Cove Springs, Florida 32043-3443, United States

HIGHLIGHTS

- Changing the electrochemical synthesis by a small amount of carbon nanotube.
- Finding optimum conditions for battery or supercapacitor.
- Controlling the film morphology and properties by controllable factors.

ARTICLE INFO

Article history:
Received 22 August 2013
Received in revised form
26 October 2013
Accepted 26 October 2013
Available online xxx

Keywords:
MnO_2
Carbon nanotubes
Electrodeposition
Manganese oxide
Supercapacitor
Lithium battery

ABSTRACT

In electrochemical synthesis of manganese oxide, current density has a substantial influence on redox behavior, but less effect on the film morphology. Here we report that a small amount (even not detectable by electron microscopy) of carbon nanotubes can significantly affect the film growth pathway. Although, the galvanostatic syntheses of manganese oxide were similar in the absence and presence of carbon nanotubes, the morphological structures are totally different. This difference is also valid for electrochemical behavior in favor of the formation of a single redox couple. The influence of carbon nanotubes on potentiodynamic electrodeposition of manganese oxide was also similar, leading to the appearance of a strong redox couple without any noticeable capacitive behavior. It should be emphasized that this influence is only valid for the experimental condition under consideration (i.e., low current densities), and electrodeposition at higher current densities in the presence of carbon nanotubes may strengthen the capacitive behavior in favor of supercapacitors (as discussed in the second part). The interesting point is that this tiny additive can predominantly control the electrochemical properties of the system under consideration: supercapacitor or battery.

1. Introduction

Manganese oxide is an important electroactive material with a vast variety of applications in various electrochemical systems, particularly electrochemical power sources. Two common types of MnO_2 are named as chemically precipitated manganese dioxide (CMD) [1–5] and electrolytic deposited manganese dioxide (EMD) [6–17]. The former method is able to control various parameters of MnO_2 by varying different experimental conditions involved in a chemical synthesis. Thus, the most attention has been paid to this method, particularly because of recent demand for the preparation of nanostructured materials. However, the latter one is of particular interest for electrochemical systems as the electroactive film covalently attaches to substrate electrode during *in situ* synthesis process. EMD has been widely employed as cathode materials for different types of batteries such as primary Zn–MnO_2 batteries [18–20], alkaline batteries [21–23], and lithium ion batteries [24–30]. A considerable attention has been paid to nanostructured manganese oxide for supercapacitors [31–37].

Due to unique properties of carbon nanotubes, they have been widely employed for the preparation of different composites made from electroactive materials to improve their electrochemical performance. There are a series of reports devoted to the fabrication of manganese oxide/carbon nanotubes composites as supercapacitors in the literature, though, the source of manganese oxide is usually CMD rather than EMD [38–40]. In this case, incorporation of carbon

---

* Corresponding author. Tel.: +1 904 297 8050.
E-mail address: eftekhari@nias.us (A. Eftekhari).

0378-7753/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2013.10.136

nanotubes within the microstructure of manganese oxide provides a nanostructure (with high specific surface area) which is needed for supercapacitors. Therefore, not only it is an active area of research to investigate electrochemical properties of CMD/carbon nanotubes composites (note that various CMDs with different electrochemical activities are available), it is of particular importance to prepare EMD/carbon nanotubes composites, as incorporation of carbon nanotubes within the solid films attached electrochemically to the substrate surface may provide practical opportunities in electrochemical systems.

In the light of recent advancements for applied purposes, some certain experimental conditions have been found for effective electrodeposition, leading to the formation of manganese oxide with desirable properties for practical performance. For instance,

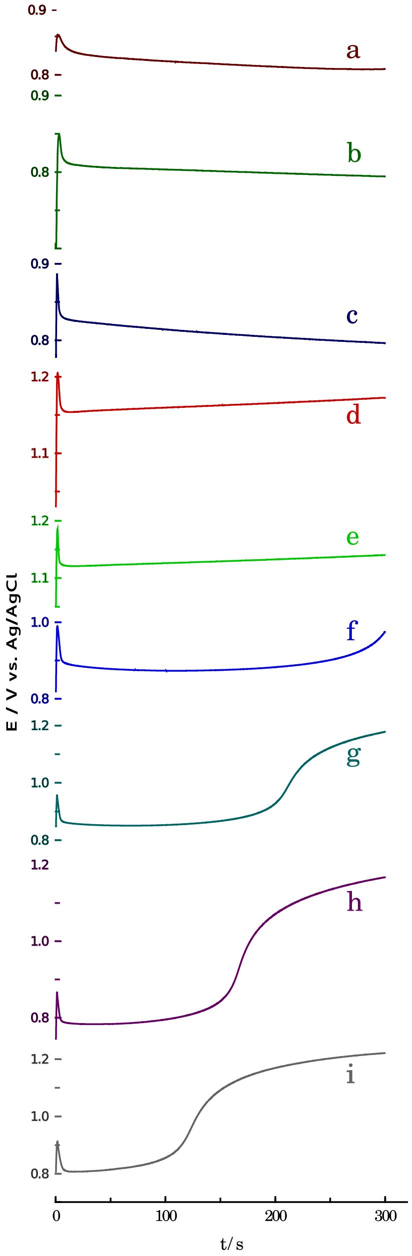

Fig. 1. Galvanostatic synthesis of manganese oxide films at different current densities: (a) 0.14, (b) 0.28, (c) 0.42, (d) 0.56, (e) 0.70, (f) 0.84, (g) 0.98, (h) 1.12, (i) 1.26, and (j) 1.40 mA cm^{-2}. The electrolyte solution was 0.5 M $MnSO_4$ + 0.5 M H_2SO_4.

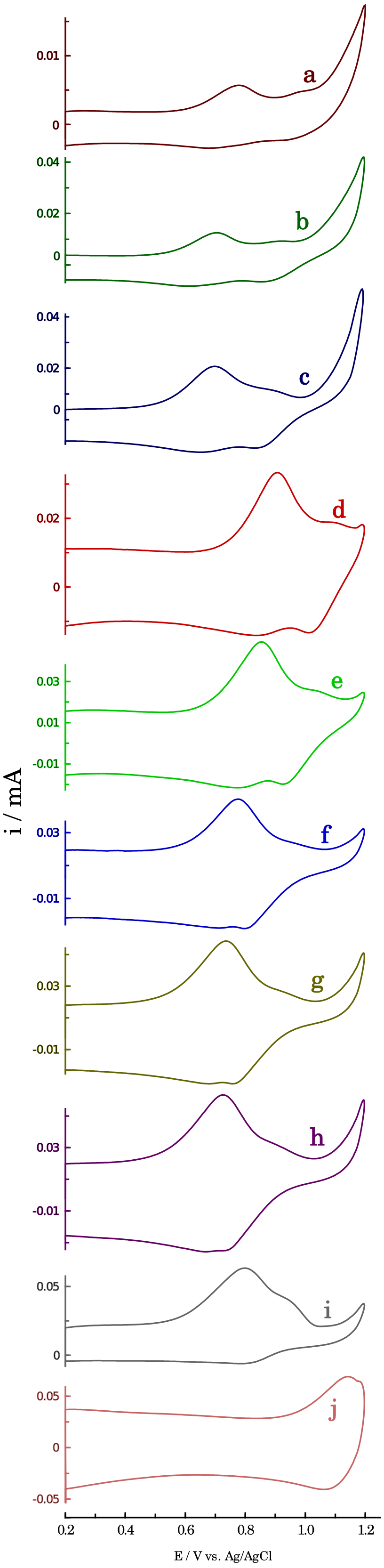

Fig. 2. Cyclic voltammetric characteristics of manganese oxide films synthesized in Fig. 1 in an aqueous solution of saturated $LiNO_3$. Scan rate 10 mV s^{-1}.