Electrochimica Acta 173 (2015) 613–618

Contents lists available at ScienceDirect

Electrochimica Acta

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

Transition metal oxide-carbon composites as conversion anodes for sodium-ion battery

Ivana Hasa, Roberta Verrelli, Josef Hassoun *

Sapienza University, Department of Chemistry, Piazzale Aldo Moro, 5, 00185 Rome, Italy

ARTICLE INFO

Article history:
Received 24 March 2015
Received in revised form 15 May 2015
Accepted 18 May 2015
Available online 21 May 2015

Keywords:
Conversion electrode
Transition-metal oxides
CuO composite anode
Sodium-ion battery

ABSTRACT

Herein, we characterize various metal oxide-carbon composites, i.e. CuO-MCMB (mesocarbon microbeads), Fe_2O_3–MCMB and NiO-MCMB, as anode materials for application in sodium-ion battery. The electrodes, supposed to react through a conversion mechanism, are studied in terms of structure, morphology and electrochemical behavior in sodium cell. The results demonstrate a specific capacity of the order of 100 mAh g^{-1} for Fe_2O_3–MCMB and NiO-MCMB, and of about 300 mAh g^{-1} for CuO-MCMB. The remarkable performance of the latter suggests the copper oxide-based electrode as the preferred anode material for battery application. Indeed, further study aimed to clarify the Na/CuO-MCMB reaction mechanism is performed by ex-situ X-ray diffraction on electrode material cast onto aluminum support. The study suggests a partial conversion reaction for CuO-based anode that is considered suitable candidate in replacement of sodium metal, in efficient and safe Na-ion battery.

1. Introduction

Since by the first commercialization in 1991, lithium ion batteries (LIBs) represented one of the most promising electrochemical energy storage systems. Light, compact and efficient LIBs are commonly diffused in portable electronics and presently considered for eventual implementation as power sources in hybrid and electric vehicles [1–3]. Recent research, focused on lithium consumption within 2012, revealed that about 27% of the lithium resources was dedicated to rechargeable lithium batteries [4]. Further study of the battery market and of the emerging application in the automotive field and in grid employment, indicated a present growing-rate of the lithium demand of about 20% per year, and estimated possible increase to about 65% of the lithium resources needed to satisfy the energy storage requirements [5]. The limited geographical localization of lithium metal resources so far led to an increase of the price and to issues concerning its long term availability, thus triggering increasing interest on alternative chemistries for energy storage application [6,7]. Room temperature sodium battery has been already studied alongside to lithium, however the better performances of the latter in terms of energy density limited the interest on sodium [8]. Recently, the identification of new, advanced electrodes for sodium battery renewed the interest on this environmentally friendly energy storage system. Indeed, the abundance of sodium and the low cost of the raw materials employed for sodium battery, as well as the active support of the well consolidated knowledge on lithium technology, accelerated its development allowing the achievement of promising results [9]. In this respect, a key role has been recently played by the identification of suitable electrode materials able to ensure enhanced electrochemical performances in terms of cycle life and delivered capacity. Promising cathode materials, mostly belonging to two principal classes of compounds, i.e. poly-anionic networks and layered oxide, have been proposed [10–13]. Poly-anionic network materials, such as $NaFePO_4$ olivine, are mainly based on sodium-insertion reaction, generally involving new phases formation [10], while layered oxides, e.g. Na_xCoO_2, react through the intercalation of sodium within the electrode structure [12]. Suitable sodium-ion battery anode, in replacement of sodium metal, represents a key requirement in order to achieve a safe energy storage system of large scale diffusion. However, the graphite-based electrodes, largely employed in lithium-ion systems, generally show issues associated with sodium ions insertion within the carbon layered structure [14,15]. Instead, amorphous carbon appears the most favorable carbonaceous material for application in sodium-ion batteries. Hard carbons, such as those obtained by glucose pyrolysis may reversibly operate upon (de-) soditation process through a *house-of-cards* mechanism [16]. However, limits concerning the low energy density of sodium-ion battery, in particular in respect to lithium-based one, due to a higher molecular weight and redox potential, are still to be solved. A significant breakthrough of the energy density of the Na-ion

* Corresponding author. Tel.: +39 0649913664; fax.: +39 064393622.
E-mail address: jusef.hassoun@uniroma1.it (J. Hassoun).

http://dx.doi.org/10.1016/j.electacta.2015.05.107
0013-4686/

battery may be achieved by using high capacity anodes, such as those based on sodium conversion electrochemical process [17,18]. Na-conversion electrodes, generally having a chemical formula MX, where M is a transition metal and X is represented by O, S or F, typically react by full reduction of the transition metal compound during the discharge process. This reaction, involving multiple electron exchange per transition metal, is characterized by a relatively high theoretical specific capacity and, consequently, conversion-based electrode materials can be considered a valid alternative to intercalation and alloying based systems. The large ionic radius of sodium, generally hindering its intercalation within layered structures, may not represent a limit in conversion-type reactions. However, problems associated to the large volume variation occurring during the electrochemical process, already observed for Na-alloying compounds, should be addressed in order to allow an efficient operation of the Na-conversion anodes. The optimization of the electrode composition, structure and morphology, as well as the use of matrixes buffering the volume variation, represent suitable strategies for the improvement of the conversion-electrode behavior in sodium cells. Few researches, with limited performances, reported on conversion electrodes suitable for effective application in sodium-ion battery [19]. Considering the large attention recently focused on sodium-based electrochemical energy storage systems, a more detailed study on this class of electrodes for sodium-ion batteries appears of great interest.

In this work we report a comparative study of conversion electrodes based on various transition metal oxides (i.e., M_aO_b where M_a=Fe, Ni, Cu) used as anode materials for sodium-ion batteries. Following the results suggested by our lithium experience [20–22], we use composite materials optimized in terms of morphology and particle size in order to investigate the suitability of the conversion reaction chemistry for sodium battery application. The metal oxides are trapped in a mesocarbon microbeads (MCMB) matrix, selected due to its suitable properties such as low specific surface area, which allows high packing and tap density and limits possible undesired side reactions. Moreover, the MCMB is used as buffering agent, limiting the huge volume stress affecting conversion materials upon cycling. This represents an important issue to address in order to avoid electrode pulverization, loss of contact and consequent cell failure. The electrodes have been characterized in sodium half-cells operating at room temperature. The CuO-based electrode, revealed as the most promising anode material, has been further investigated, by using X ray diffraction

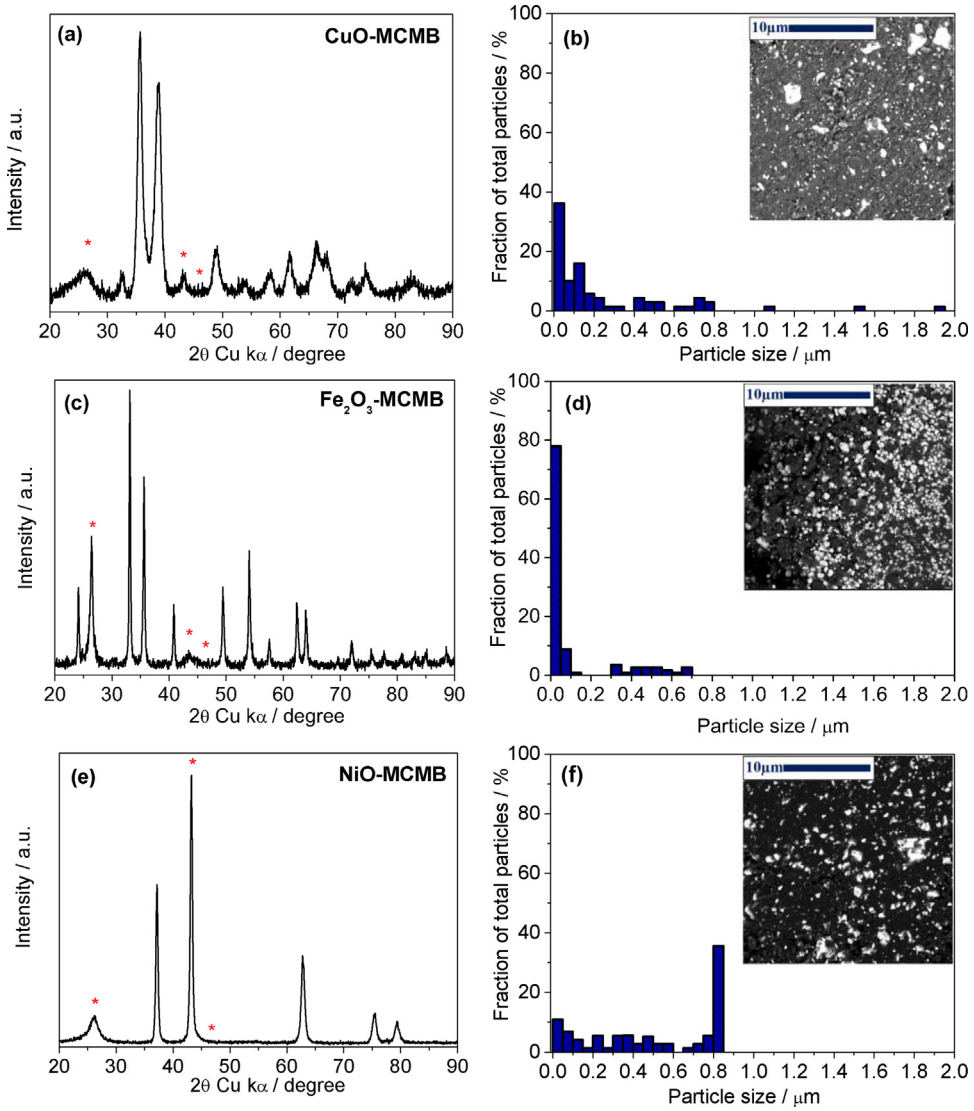

Fig. 1. X-ray diffraction patterns, particle size distribution plots and corresponding scanning electron micrographs (insets) of CuO-MCMB (a,b), Fe_2O_3-MCMB (c,d) and NiO-MCMB (e,f) powder samples. The main diffraction peaks of the MCMB phase (JCPDS# 75-2078) are marked by red asterisks.