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Electrochemical activity of electrode material consisting of porous copper and silica aerogel

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Abstract

Electrochemically obtained copper was combined with silica aerogel (SiO_{2ag}). Obtained composite (SiO_2@Cu/Cu_xO_y) was tested as an electrode in contact with $LiPF_6$ in EC/DMC electrolyte. The electrochemical measurements showed the presence of complex redox couple activities of SiO_2@Cu/Cu_xO_y.

This experiment was employed to help in understanding the carbon role used as an electric contact for silica in Li-Ion batteries and clarify the electrochemical process of lithium insertion into material. Studies allowed to explain the function of each component in electrode reaction of SiO_2@Cu/Cu_xO_y in contact with aprotic solvent.

Keywords: silica, copper, copper (II) oxide, lithium, cyclic voltammetry

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1. Introduction

An extensive research activities have been directed to develop rechargeable lithium – ion batteries with large capacity, high power and long cycling life. Nowadays anode materials for Li-Ion batteries have attracted attention worldwide.

Silica is one of recently introduced candidate for anode material. Specially manufactured nanosized SiO_2 is found to exhibit high practical charge capacity extending theoretical capacity of carbonaceous anodes [1-3]. Nanosilica is polarized being in contact with carbonaceous conducting binder [4,5].

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Here we propose copper as a binder. The aim is to check if SiO_2 reduction to lithium silicate and silicon requires inserted lithiated carbon as a conductivity additive (LiC_6), or faradaic reaction may take place without presence of carbonaceous binder.

2. Experimental

Material preparation

Copper was obtained in electrochemical reaction between aluminium (Al) and copper (II) chloride ($CuCl_2$). In this reaction oxidized aluminium loses e^-, becoming Al^{3+} and the reduced copper ions forms very fine solid copper precipitate. Copper surface is partially oxidized in atmospheric air. This material was mixed with silica aerogel (5% wt.) on agate mortar and pestle to obtain uniform consistence. Silica aerogels were obtained by commonly known method described in literature [6-8]. Powder was pressed on manual hydraulic press (Specac Ltd.) for about 30 seconds with a load of 10.2 GPa on 5 mm diameter matrix (Specac Ltd.) and used as a working electrode in Swagelok® type cells vs. Li (lithium foil 99.9% purity, 0.75mm thickness, AlfaAesar) with 1 $LiPF_6$ dissolved in mixed solvent, which was composed of the equal volumetric amount from both Ethylene Carbonate (EC) and Dimethyl Carbonate (DMC) (LP30 Merck, Germany) as the electrolyte. Obtained disc shaped electrodes from $SiO_2@Cu/Cu_xO_y$ were dried under dynamic vacuum in an oven (Glass Oven B 585 Büchi, Germany) for 24 h at 80ºC. The cells comprising $SiO_2@Cu/Cu_xO_y$ as a working electrode and lithium disc as a counter electrode with lithium wire as a reference electrode were assembled in an argon-filled Lab Star glove-box workstation (MBraun). Oxygen and water level in the glove box were maintained below 0.5 ppm.

2.2. Morphology

The morphology of the sample was determined using a scanning electron microscope (SEM, Carl Zeiss AG, Germany) equipped with an EDX detector (EDS BRUKER AXS Quantax 200, Germany).

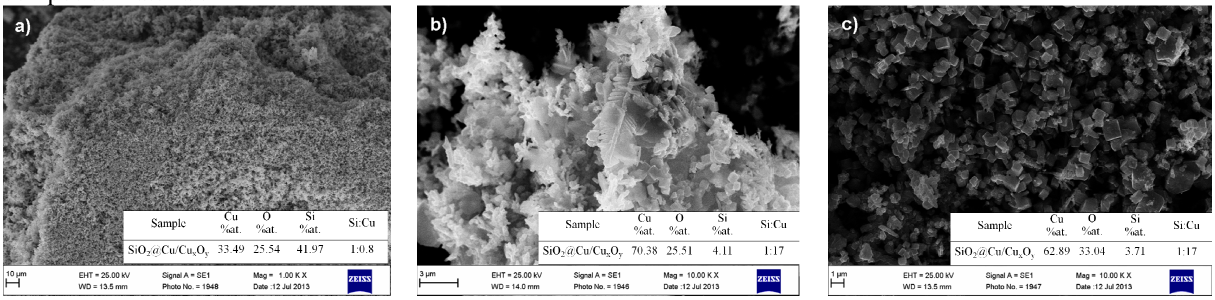
2.3. Electrochemical measurements

Cyclic voltammetry was performed using an electrochemical workstation Autolab (PGStat302N) between 0.02–3.1 V versus Li/Li^+ at a scan rate of 100 μVs^{-1} and also between 0.02-1.947 V vs. Li/Li^+ at a scan rate 1 mVs^{-1}. All measurements were done at 21 (±1) °C.

3. Results and Discussion

3.1. Morphology

Scanning electron microscopy was applied to study morphology of the materials. Images of $SiO_2@Cu/Cu_xO_y$ material at different magnification are shown in Fig. 1. Fig. 1a, 1b and 1c demonstrate heterogeneous structure of the composite material.



Sample	Cu %at.	O %at.	Si %at.	Si:Cu
$SiO_2@Cu/Cu_xO_y$	33.49	25.54	41.97	1:0.8

Sample	Cu %at.	O %at.	Si %at.	Si:Cu
$SiO_2@Cu/Cu_xO_y$	70.38	25.51	4.11	1:17

Sample	Cu %at.	O %at.	Si %at.	Si:Cu
$SiO_2@Cu/Cu_xO_y$	62.89	33.04	3.71	1:17

Fig. 1. SEM images of the $SiO_2@Cu/Cu_xO_y$ with elemental analysis from EDX.

In the pictures we may see silica aerogels typical interconnected porous network as it is described in Ref. [8,9], (see Fig. 1a). Moreover, the structure of aerogel is highly cross-linked. Fig 1b illustrates SEM image of Cu particles which creates the agglomeration of smaller particles, with dendrite like structured domain [10]. In Fig. 3c the well defined cubic structure of particles of an average size ~500 nm are shown. The shape and size of these particles is typical that was observed for copper/copper (II) oxide micro-crystals as it is given in Ref. [11].

The Tables in the inset of SEM pictures represents EDX elemental analysis and Si:Cu ratio. Taking into consideration that material is heterogeneous we cannot examine the sample as a whole. The EDX analysis is taken from different parts of the sample. Thus, one may expect that the obtained results are crude estimation of the material's composition.

3.2. Characterization of SiO_2@Cu/Cu_xO_y electrode

Cyclic voltammetry curves of silica using copper as a binder in the potential range of 0.02 and 3.1 V (versus Li/Li$^+$) at a scan rate of 100 μVs^{-1} and in the potential range of 0.02 and 1.947 V (versus Li/Li$^+$) at a scan rate of 1 mVs^{-1} are shown in Fig. 2.

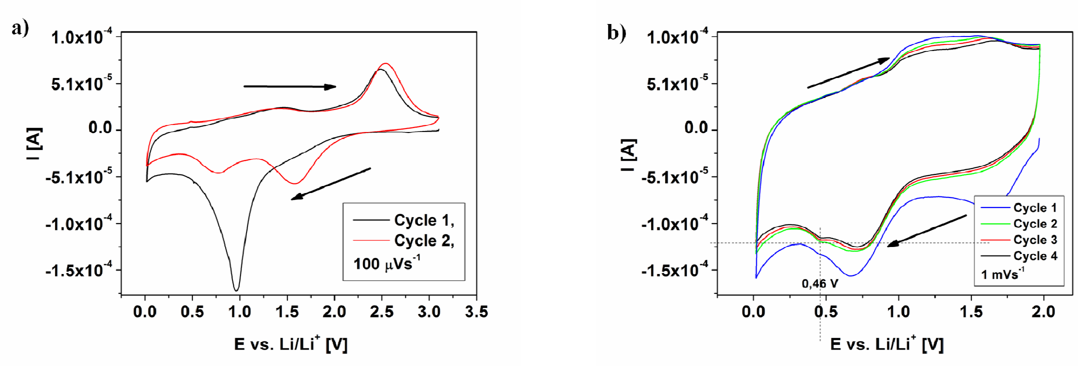


Fig. 2 Cyclic voltammetry curves of SiO_2@Cu/Cu_xO_y electrode material (a) in the potential range of 0.02 and 3.1 V (versus Li/Li$^+$) at a scan rate of 100 μVs^{-1} (b) in the potential range of 0.02 and 1.947 V (versus Li/Li$^+$) at a scan rate of 1 mVs^{-1},

In Fig. 2a the first two CV curves are shown followed next 4 CV curves in Fig. 2b. The first CV curve of the material (black line, Cycle 1) exhibits cathodic current maximum at potential $E = 0.96$ V. The reduction process is related to solid electrolyte interface (SEI) formation and overlaps with lithium intercalation into Cu_xO_y as it was previously reported by Sun *et.al.* for nanoribbons of CuO [12]. The extraction process of lithium ions from the electrode material occurs at potential $E \approx 2.5$ V and is attributed to CuO and Cu_2O formation. The cathodic maxima at potentials 1.59 and 0.79 V, seen for the second cycle, correspond to the multistep electrochemical lithium reaction process with formation of Li_2O and Cu_xO_y for former and Cu and Li_2O for latter potential [13]:

$$\mathrm{CuO} + \mathrm{xLi}^{+} + \mathrm{xe}^{-} \rightarrow \left[\mathrm{Cu}^{\mathrm{II}}_{1-\mathrm{x}}\mathrm{Cu}^{\mathrm{I}}_{\mathrm{x}}\right]\mathrm{O}_{1-\mathrm{x}/2} + \mathrm{x}/2\mathrm{Li}_2\mathrm{O} \tag{1}$$

$$\left[\mathrm{Cu}^{\mathrm{II}}_{1-\mathrm{x}}\mathrm{Cu}^{\mathrm{I}}_{\mathrm{x}}\right]\mathrm{O}_{1-\mathrm{x}/2} + \mathrm{xLi}^{+} + \mathrm{xe}^{-} \rightarrow \mathrm{Cu} + \mathrm{x}/2\mathrm{Li}_2\mathrm{O}_{2/\mathrm{x}-1} \tag{2}$$

The structure of copper oxide is preserved while copper ions undergo progressive reduction from Cu(II) to Cu(I) with the formation of oxygen vacancies. Further reduction leads to Cu formation incorporated into Li_2O matrix [13].

At potential lower than 0.8 V lithium reaction with silica [1,3,5] as well as lithium insertion into copper oxide [11,13] may occur. Thus, for SiO_2@Cu/Cu_xO_y system two independent electrochemical processes may appear and overlap. To distinguish this phenomenon the SiO_2@Cu/Cu_xO_y electrode was cycled in the potential range from 0.02

to 1.95 V. In Fig 2b subsequent cycles with two cathodic peaks at 0.70 and 0.46 V are seen. The first maximum is broad and is assigned to Li^+ intercalation into CuO [13,14]. The second peak is small, sharp and might be related to lithium ion reaction with SiO_2 with formation of lithium silicate and silicon. The cathodic peak (E = 0.46 V) is not seen in Fig. 2a as the material needs to be charged to 1 mV at least two times with low sweep rate. However, it is difficult to clearly confirm assumption of silica reduction as Sohn *et.al.* claim that silica reacts with lithium in the potential range below 0.3 V [5]. It may be also confusing as other Authors did not observed any cathodic peaks below 0.3 V after second or later cycles [1,3,4].

On the anodic branch the broad maximum is seen at ~ 1.1 V. It is supposed that reaction taking place at this potential (1.1 V) comes from extraction process of lithium ions from lithium silicate [3] and Cu_xO_y system [13]. The processes are very complex and at this level we are not able to clarify this phenomenon. We are aware that further studies are required.

4. Summary

Electrochemically obtained copper has been used to prepare SiO_2@Cu/Cu_xO_y composite anode material. Material is not homogenous in micro scale. It is rather a complex system consisting of silica, copper and copper oxide acting as one electrode material. Such material has been received to distinguish lithium insertion into silica and/or copper oxide.

Cyclic voltammetry was performed between 0.02 - 3.1 V versus Li/Li^+ at a scan rate of 100 μVs^{-1} and also between 0.02 - 1.947 V vs. Li/Li^+ at a scan rate 1 mVs^{-1}. The second range was executed to identify electrochemical process occurring at the potentials below 0.5 V. It was found that cathodic maxima at 0.70 and 0.46 V were attributed to lithium reaction with copper oxide and silica, respectively.

Cyclic voltammetry obtained for composite material give evidence of faradaic activity of used material. Silica undergoes faradaic reduction with copper/copper oxide binder instead of the presence of carbonaceous support.

Further investigation including the usage of metallic copper obtained under reduce atmosphere should allow to clarify the activity of carbon and silica more precisely.

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