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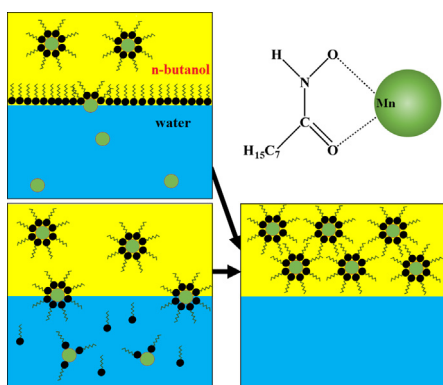
Application of octanohydroxamic acid for liquid-liquid extraction of manganese oxides and fabrication of supercapacitor electrodes

J. Milne, I. Zhitomirsky*

Department of Materials Science and Engineering, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4L7, Canada



GRAPHICAL ABSTRACT



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ABSTRACT

MnO_2 and Mn_3O_4 particles were prepared by wet chemical methods and efficiently dispersed and mixed with multiwalled carbon nanotubes (MWCNT) for the fabrication of composite MnO_2 -MWCNT and Mn_3O_4 -MWCNT electrodes for electrochemical supercapacitors (ES). The problem of particle agglomeration was addressed by particle extraction through a liquid-liquid interface (PELLI) using octanohydroxamic acid (OHA) as a new extractor. OHA exhibited remarkable adsorption on particles due to a bidentate bonding mechanism. The use of OHA broadened the application of PELLI technology, because it allowed good extraction of particles from an aqueous phase at high pH. Moreover, OHA allowed efficient extraction by strong adsorption on particles not only at the liquid-liquid interface, but also in the bulk of an aqueous phase. Building on the advantages offered by the PELLI method and OHA as an extractor we found that Mn_3O_4 -MWCNT electrodes exhibited a remarkably high capacitance of 4.2F cm^{-2} . Another major finding was that capacitance of Mn_3O_4 -MWCNT electrodes was higher than that of MnO_2 -MWCNT electrodes at active mass of 33 mg cm^{-2} . This finding showed processing advantages of PELLI and paved the way for applications of novel colloidal and surface modification strategies for the development of advanced ES. A conceptually new approach has been proposed based on the use of hydroxamic acids as capping agents for synthesis and extractor molecules for PELLI.

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1. Introduction

Aqueous synthesis techniques are widely used for the fabrication of metal oxide and hydroxide particles, quantum dots and

* Corresponding author.

E-mail address: zhitom@mcmaster.ca (I. Zhitomirsky).

nanoparticles of metals [1–5]. In many applications [6–10], the particles formed in an aqueous phase are transferred to an organic solvent, containing dissolved polymers and other functional components for the fabrication of composite materials. The use of polymers, which are soluble only in organic solvents, facilitates the fabrication of composites for applications in devices with improved moisture stability. The use of organic solvents is critical for the manufacturing of materials and devices, which require stable operation in aqueous environment, such as electrodes of supercapacitors and batteries, protective coatings, implants and other composite materials and devices containing water insoluble polymers as binders or functional components [11,12]. Organic solvents offer many advantages for tape casting and other colloidal techniques, due to superior binding properties of polymers that are soluble in organic solvents, compared to water soluble polymer binders. Organic solvents are beneficial for various film deposition methods, such as spin casting [13], electrophoretic deposition [14,15], spray deposition [16] and dip coating [17]. Therefore, for many advanced applications the particles formed in an aqueous phase must be washed, dried and then re-dispersed in an organic phase. However, drying procedure introduces problems related to particle agglomeration. The reduction of surface energy of particles and condensation reactions of surface OH groups are major reasons of the agglomeration.

Particle extraction through liquid-liquid interface (PELLI) [18] provides the capability of transferring particles from an aqueous synthesis medium directly to an organic phase, thus avoiding the drying procedure and agglomeration of the particles. Studies in this area focused on the development of extractor molecules with specific anchoring groups, selection of receiving solvents and development of new extraction mechanisms. Nanoparticles of gold [19,20], silver [21] and quantum dots [22] were transferred to organic media using fatty acid, alkanethiol and alkylamine molecules as extractors. Fatty acids were investigated for the extraction of magnetite [23]. Various co-solvents were used in order to enhance the extraction efficiency [22,24]. The extraction mechanisms involved various extractor-particle interactions, such as covalent [20,21], electrostatic [25] and ion-pair interactions [26].

PELLI is especially attractive for agglomerate free processing of oxide and hydroxide materials. A relatively recent development is the application of lauryl gallate [27–29] and alkylphosphonic acids [29–31] for the extraction of metal oxides and hydroxides. These new extractors offered an advantage of strong polydentate bonding to the particle surface. Top-down and bottom-up PELLI methods were developed [18]. In another approach [18,28,32] particles were modified in-situ during synthesis with aldehyde molecules, containing anchoring catechol groups and then in a Schiff base formation reaction with extractor molecules at the interface of two immiscible liquids. From these prior investigations, it appears that PELLI can be used for the development of advanced metal oxide-polymer nanocomposites.

The choice of anchoring groups of the extractor molecules plays a crucial role in controlling the extractor adsorption on particles. So far PELLI was applied to a limited number of oxide materials. It is important to note that alkanethiols do not adsorb on the surfaces of oxides [33]. Fatty acids and alkylphosphonic acids showed relatively weak adsorption on oxides [33]. The important task is to develop a larger pool of extractor molecules and find more efficient extractors, which allow strong adsorption on various inorganic materials for PELLI applications. Understanding the extraction mechanisms and development of new extraction strategies are critical factors for the further advances in the PELLI methods.

The goal of this study was the application of octanohydroxamic acid (OHA) as a new extractor for PELLI and analysis of fundamen-

tal extraction mechanisms. Another target of this investigation was the application of OHA as an extractor in the PELLI method for the development of ES. We explored different extraction strategies and proposed extraction mechanisms. In contrast to previous studies, which involved the lauryl gallate and alkylphosphonic acids adsorption on particles at the interface of two immiscible liquids, we found that OHA can penetrate the interface. We provided experimental evidence that OHA adsorbed on the particles not only at the interface but also in the bulk of an aqueous phase. This finding indicated that long chain extractors from the hydroxamic acid family can potentially be used as capping agents for synthesis in an aqueous phase and extractors in the PELLI method. We discussed benefits of OHA and related molecules for the fabrication of advanced nanocomposites by PELLI method. Another important finding of this investigation was the development of advanced ES electrodes. The experimental results described below indicated that OHA allowed efficient extraction of MnO_2 and Mn_3O_4 and fabrication of composite electrodes, which showed promising performance for ES applications.

2. Experimental procedures

Reagent grade purity KMnO_4 , $\text{Mn}(\text{NO}_3)_2$, poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVB, average Mw = 50,000–80,000), NaOH, *n*-butanol (Aldrich, Canada), octanohydroxamic acid (OHA) (TCI America) were used. Multiwalled carbon nanotubes (MWCNT, ID 4 nm, OD 13 nm, length 1–2 μm , 98% purity) were supplied by Bayer, Germany. Ni foams with 95% porosity were provided by Vale Limited Company.

For the fabrication of MnO_2 particles, 1 g KMnO_4 was dissolved in 30 mL of water and then 20 mL of *n*-butanol was added. The reduction of Mn^{7+} species by *n*-butanol [27] resulted in the formation of MnO_2 particles, which precipitated in the aqueous phase. The procedure for synthesis of Mn_3O_4 particles was described in a previous investigation [28]. OHA was used as a new extractor for PELLI method. The MnO_2 and Mn_3O_4 particles, synthesized in aqueous solutions, were transferred to *n*-butanol using OHA as an extractor.

The suspensions for electrode fabrication contained 80% MnO_2 or Mn_3O_4 , extracted from the aqueous phase, and 20% MWCNT in *n*-butanol. PVB binder, dissolved in ethanol was added to the mixture, the PVB content was 3% of the total mass of the MnO_2 -MWCNT or Mn_3O_4 -MWCNT electrodes. The obtained slurries were used for the impregnation of Ni foam current collectors. The total mass of the impregnated material was 33 mg cm^{-2} . Materials characterization and electrochemical testing techniques were described in previous investigations [28,34].

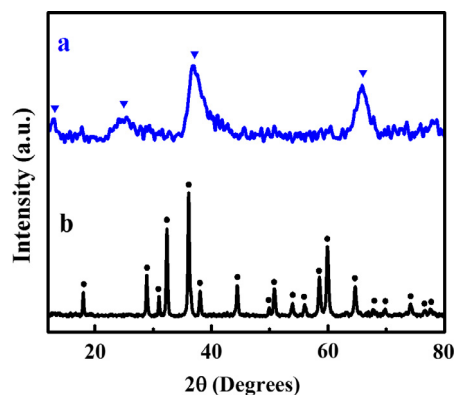


Fig. 1. X-ray diffraction patterns of (a) MnO_2 (▼-JCPDS file 00-023-1046) and (b) Mn_3O_4 (●-JCPDS file 04-007-1841).

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