



Research paper

Electrochemically synthesized cobalt redox active layered double hydroxides for supercapacitors development



Ylea Vlamidis^a, Erika Scavetta^a, Marco Giorgetti^a, Nicola Sangiorgi^{b,c}, Domenica Tonelli^{a,*}

^a Department of Industrial Chemistry “Toso Montanari”, ALMA MATER STUDIORUM-University of Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy.

^b Institute of Science and Technology for Ceramics-National Research Council of Italy (CNR-ISTEC), Via Granarolo 64, 48018 Faenza, Italy.

^c Department of Chemical Science and Technology, University of Rome Tor Vergata, via della Ricerca Scientifica, 00133 Rome, Italy.

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ABSTRACT

This paper describes the electrosynthesis and characterization in alkaline solutions of two layered double hydroxides (LDHs) containing Co as divalent cation and Al or Fe as trivalent one on Pt supports. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) experiments demonstrated a capacitive behaviour. LDHs containing Al³⁺ or Fe³⁺ displayed different responses, highlighting a key role of the trivalent metal. High specific capacitances calculated from charge-discharge experiments at a current density of 1 A g⁻¹, were displayed by the two materials and resulted 854 and 869 F g⁻¹ for the Al or Fe containing LDH, respectively. The long-term cycling capability was also investigated giving satisfactory results.

The presence of Fe improves the performance of the LDH as pseudocapacitor, especially to achieve better performances in terms of energy and power densities. In view of the development of low cost supercapacitors preliminary tests aimed to deposit Co based LDHs on a large area graphite substrate were also successfully carried out.

1. Introduction

Electrochemical capacitors, also called supercapacitors, have attracted increasing interest over the past few years due to their potential to deliver high power density in a very short time, their excellent cyclability (Zhai et al., 2011), the short charging time if compared with batteries, and their ability to store more charge than conventional capacitors. These qualities explain the renewed interest for such electrochemical devices in different domains such as digital telecommunication systems, power supplies for computers, and electric/hybrid vehicles (Miller and Burke, 2008; Simon and Gogotsi, 2008). Based on the charge storage mechanisms, the supercapacitors can be classified into two categories, namely electrical double-layer capacitors (EDLCs) and pseudocapacitors, also known as redox-capacitors. EDLCs store charge by adsorption of electrolyte ions onto the surface of electrode materials, whereas in the case of pseudocapacitors the capacitance arises from fast and reversible redox reactions (of Faradic nature) occurring at or near the electrode surface (Kötz and Carlen, 2000). Traditional pseudocapacitive materials are RuO₂ and MnO₂ (Zhang et al., 2014) but the list also includes conducting polymers (Wang et al., 2012) like polyaniline, polypyrrol and polythiophene or other transition metal oxide/hydroxides such as Fe₃O₄ (Wang et al., 2014b), NiO

(Sun et al., 2014), MoO₃ (Mendoza-Sánchez et al., 2013), Co₃O₄ (Che and Liu, 2015), Ni(OH)₂ (Huang et al., 2014), Co(OH)₂ (Wang et al., 2012). Pseudocapacitors based on transition metal oxides exhibit much higher specific capacitance than those based on carbon materials and conducting polymers, as they can provide a variety of oxidation states for an efficient redox charge transfer (Wang et al., 2012). Layered double hydroxides (LDHs) containing transition metals have been widely investigated since they are very promising materials for a large number of possible applications due to their versatility, tunable properties, wide range of compositions and low cost (He et al., 2015; Wang et al., 2015; Tang et al., 2016). Recently, due to their peculiar properties such as efficient anion exchange capacity, high redox activity and low-cost, LDHs have been considered as alternative pseudocapacitive materials (Abellán et al., 2014; Chen et al., 2014; Ge et al., 2014; Wang et al., 2014a; Vialat et al., 2015b; Ma et al., 2016). These materials can be synthesized by several chemical routes (Rives, 2001; Theiss et al., 2016). In the last few years our group has optimized an electrochemical approach in order to obtain LDH films on any kind of conductive supports (Scavetta et al., 2007; Scavetta et al., 2014; Li et al., 2014; Gualandi et al., 2015b). The electrodeposition can be considered as a simple, low cost and fast method of synthesis that also controls the thickness of deposited films (Gualandi et al., 2015a). The

* Corresponding author.

E-mail address: domenica.tonelli@unibo.it (D. Tonelli).

method is based on the electrochemical production of hydroxide anions necessary to induce the LDH precipitation by cathodic reduction of nitrate ions (Scavetta et al., 2014). Recently, these materials have been also investigated as water splitting catalysts to gain more insight on the effect of the substitution of Al with Fe as trivalent metal on their catalytic performance (Vlamidis et al., 2016). In this paper the electrochemical properties of LDHs, containing Co as the redox active center and Al or Fe have been studied in alkaline solution, using Pt as the electrode support. The research has permitted to find out the specific capacitance improvement for the Fe/Co based LDH in respect to the Al containing clay. Eventually, preliminary tests conducted on Co/Fe LDH deposited on a large area graphite substrate have been also carried out.

2. Materials and methods

2.1. Chemical equipment

The electrochemical deposition and characterization were performed by using an Autolab PGSTAT20 (Ecochemie, Utrecht, The Netherlands) potentiostat/galvanostat controlled by a personal computer via GPES 4.9 software (Windows operating system).

All electrochemical experiments were carried out using a single compartment, three-electrode cell. A Pt disk (0.5 cm diameter when performing the CV characterization and charge/discharge experiments, and 0.2 cm diameter when performing the EIS measurements) or flexible graphite sheets (Grafoil grade GTJ purchased by VED S.r.l.) were used as working electrodes and a platinum wire (Sigma Aldrich) as counter electrode. A saturated calomel electrode (SCE) was the reference electrode during the electrochemical treatment of the conductive supports and the deposition of the LDHs, while an Hg/HgO electrode was used as reference during the characterizations and the performances study of the investigated materials in basic media. Both electrodes were purchased from Amel Instruments. All the potentials were referred to the reversible hydrogen electrode (RHE), unless otherwise specified, according to $E_{vs\ RHE} = E_{vs\ SCE} + 0.0592\ pH + 0.241$.

Electrochemical Quartz Chrystal Microbalance (EQCM) experiments were performed using a MAXTEK PM-710 device, connected to the Autolab potentiostat. The probe was equipped with a 5 MHz AT-cut quartz crystal coated with sputtered Pt (surface area $1.37\ cm^2$). The EQCM experiments were repeated 3 times in order to verify the reliability of the values.

The morphology and the chemical compositions of LDH films were investigated by FE-SEM LEO 1525 ZEISS instrument fitted with an EDS detector, working with an acceleration voltage of 15 keV.

A PHI 5000 Versaprobe II Scanning X-ray Photoelectron Spectrometer, equipped with a monochromatic Al K-alpha X-ray source (1486.6 eV energy, 15 kV voltage and 1.0 mA anode current), was used to investigate the surface chemical composition. The samples were prepared on Pt electrode plates (geometric area = $1\ cm^2$), performing 10 electrodeposition steps at the same electrode (total deposition time of 300 s). The entire electro-coated surface was used in order to collect the photoelectron signal. All the spectra were analyzed by using the Casa XPS software. Peaks shifts were normalized with the C 1 s peak set at 284.5 eV and after calibration the background from each spectrum was subtracted using a Shirley-type background.

2.2. Chemicals

Cobalt(II) nitrate hexahydrate (98% pure), aluminum nitrate nonahydrate (> 96%) and sodium hydroxide (98%) were supplied by Sigma-Aldrich. Iron(III) nitrate nonahydrate (99% pure) and sulfuric acid (95–98% w/w) were purchased from Riedel-de Haën and J. T. Backer, respectively. The supporting electrolyte for all the electrochemical experiments was NaOH at two different concentrations, i.e., 0.1

and $1.0\ mol\ L^{-1}$. The LDHs were electrosynthesized from freshly prepared solutions of the metal nitrates in doubly distilled water.

2.3. Preparation of Pt and graphite modified electrodes

The pretreatment of Pt electrodes is extremely important in order to achieve a well adherent coating (Gualandi et al., 2012) so the Pt surface was prepared according to the following procedure.

The Pt surface was polished to a mirror-like surface first by a mechanical cleaning, using sand-paper and aqueous alumina ($0.05\ \mu m$) slurry on a wet polishing cloth, and then the electrode was submitted to two electrochemical treatments. First 250 cycles between $-0.25\ V$ and $+1.30\ V$ vs SCE were performed in $0.1\ M\ H_2SO_4$ at the scan rate of $1\ V\ s^{-1}$. Afterwards the electrode was polarized at the potential of $-0.90\ V$ vs SCE for 300 s (under stirring in order to remove hydrogen bubbles) in $1.0\ M\ H_2SO_4$, followed by 3 CV cycles between $-0.25\ V$ and $+1.30\ V$ vs SCE in $0.1\ M\ H_2SO_4$.

The LDH films were deposited on the electrode surface by cathodic reduction of a $0.03\ M$ solution containing Co(II) and M(III) at a molar ratio of 3:1. The electrochemical reaction was carried out by applying a fixed potential ($-0.90\ V$ vs SCE) for 30 s. After performing the modification, the electrode was immediately rinsed with water.

Graphite sheets were cut into slices of $2 \times 1\ cm$ size, and then the supports were soaked in ethanol for 30 min under sonication, using a Bandelin Sonorex Super Sonicator (RK 510H). The electrical contact was realized by using adhesive copper foil and then the geometric area of the electrode was limited to $1\ cm^2$ using nail polish. After this procedure the electrodes were dried in oven at $60\ ^\circ C$ for 36 h. The electrodeposition was again carried out in potentiostatic conditions ($-1.1\ V$ vs SCE) for 30 or 120 s using the solution containing the nitrate salts of Co(II) and Fe(III) or Al. Finally, the modified electrodes were rinsed with water and dried again for 48 h. For the graphite coated electrodes the amount of deposited Co/Fe LDH was determined by means of a six digit analytical balance. The obtained values were 20 and $80\ \mu g\ cm^{-2}$ for 30 and 120 s deposition times, respectively.

2.4. Electrochemical measurements

Electrochemical measurements were conducted in alkaline solution (0.1 and $1.0\ M\ NaOH$). The specific capacitance of the electrodes coated with the LDHs was investigated by cyclic voltammetry and recording galvanostatic charge-discharge curves at the current densities of 1.0, 2.5, 5.0, and $10.0\ A\ g^{-1}$. The EIS dispersions were performed using a CHInstruments Model 660A (Austin, TX) controlled by a personal computer via CHInstruments software. All the EIS dispersions were recorded in the range $1\ mHz$ – $100\ kHz$ and the temperature was controlled with a Julabo MB-5 thermostat. Impedance spectra were fitted by the Z-View software.

3. Results and discussion

3.1. Physical characterization of the LDH films deposited on Pt

The structures of the LDH films were confirmed by recording the XRD patterns, and since the reproducibility of the electrosynthesis is quite good, we refer to what was already published as to this characterization (Vlamidis et al., 2016).

The mass of the LDHs deposited on Pt during the electrosynthesis was determined by EQCM experiments. Fig. 1 displays the massograms recorded throughout the potential pulse for the two LDHs. As previously demonstrated (Gualandi et al., 2015b), for Co/Al LDH the mass grows very quickly during the first 10 s of application of the cathodic potential and then remains nearly constant when the precipitation of the material in the bulk solution starts to occur. Co/Fe LDH shows a similar trend but the growth lasts for 15 s, leading to a greater amount of the deposited clay and thus evidencing a possible key role played by

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