

CARBON/LAYERED DOUBLE HYDROXIDE COMPOSITES FOR CAPACITOR USE

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Introduction

LDHs are a class of ionic lamellar compounds that consist of positively charged host layers with two kinds of metallic cations and exchangeable hydrated anions located in the interlayer gallery for charge balance. The charge of the layers arises from the substitution of a part of the divalent metal ions with trivalent ones. Metal ions are octahedrally coordinated by six oxygen atoms belonging to six OH groups. Each OH group is shared by three octahedral cations [1,2]. The general formula is $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{+n}(A^{n-})_x \cdot nH_2O$ where M^{2+} indicates divalent cation (Mg^{2+} , Fe^{2+} , Co^{2+} , etc.), M^{3+} - trivalent cation (Al^{3+} , Fe^{3+} , Cr^{3+} , etc.), A^{n-} -interlayer anion and x is equal to the molar ratio $M^{3+}/(M^{3+}+M^{2+})$. The parent material of those compounds is the naturally occurring mineral hydroxalite, which has the formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$. Due to some interesting properties [1,3] these compounds have been extensively studied for many possible applications [1-4]. In the field of electrochemistry they have been applied as electrode for alkaline secondary cells [5] and materials for electrodes in asymmetric capacitors [6]. In the present study for the first time LDHs have been used as a source of metal oxide for reversible faradaic reactions in composite with activated carbon. Synthesis of LDH/carbon composite has been achieved through co-precipitation under refluxing conditions from solution containing a proper amount of metal salts, urea and activated carbon. In this approach, the carbon surface active sites and defects serve as nucleation centers for the growth of LDH crystallites during precipitation. Synthesis of LDHs was followed by thermal treatment at different temperatures in synthetic air. During annealing LDHs were converted to a composite consisting of mixed metal oxides and, depending on the temperature, carbon residue.

Experimental

Steam activated carbon material was supplied by NORIT. Urea, cobalt nitrate and aluminum nitrate were commercially available reagents (*p.a.*) from Aldrich® and Fluka®.

LDH/carbon composite was prepared via a method of homogenous precipitation described previously in [7] except replacing chlorides with nitrates. Briefly, 1000cm³ of water solution containing proper amount of $Co(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, urea and activated carbon was heated at 95°C and under continuous magnetic stirring for 48h. After filtering and washing with distilled water and ethanol for several times,

the resulting powder was dried at 80°C overnight. This material is denoted as RCoAU (R-activated carbon, Co, A – cobalt and aluminium, respectively, U- urea). Synthesis of LDHs was followed by thermal treatment in synthetic air (10 l/hour) for 3 hours at different temperatures ranging from 160 to 500°C. Samples after heat treatment are denoted as RCoAU_x where letters correspond to the carbon composite and x ($x=200, 300$ etc.) is the temperature of heat treatment.

A detailed physical characterization (X-ray, SEM, TEM, nitrogen sorption) of prepared composites was performed. Capacitor performance of the composite electrodes was studied by different electrochemical techniques.

Results and Discussion

The simplest and most commonly used preparation method is co-precipitation of the chosen M^{2+} and M^{3+} hydroxides with diluted NaOH and/or Na_2CO_3 or $NaHCO_3$. In this paper, for the preparation of carbon/LDH composite, urea method was chosen because of its advantages comparing to the co-precipitation technique. In the synthesis with urea (on the contrary to synthesis with addition of base during processing) the controlled supply of carbonate and hydroxide by the decomposition of urea in the presence of M^{2+} and M^{3+} salt mixture successfully leads to the formation of monodisperse hydroxalite particles with good crystallinity degree and a narrow distribution of particle size. SEM images of the as-received LDH/carbon composite (Fig. 1) confirmed uniform and hexagonal plate-like particles of LDH well dispersed on the carbon material external surface. These particles, with the size of about 5µm, have roughly hexagonal shapes and more or less sharp edges. Existence of Co and Al has been confirmed by energy dispersive analysis of the X-ray spectrum which indicated presence of ~15 % of Co.

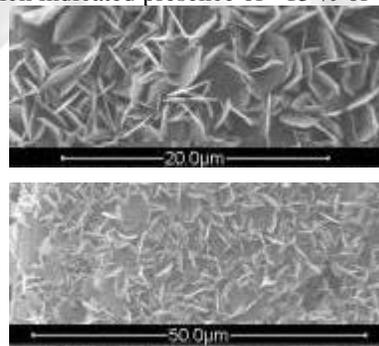


Fig. 1 SEM images of the composite RCoAU consisting of LDH particles dispersed on the surface of activated carbon.

LDH particles have been deposited onto the surface of activated carbon and some particles also could fill in the inner big pores or block the smaller pores of activated carbon. This suggestion matches well with the results of nitrogen sorption measurements which are presented in Fig. 2. From the obtained curves it is clearly seen that material changes from micro to mesoporous after co-precipitation. Specific surface area calculated with BET equation decreases from 1720 m²g⁻¹ for carbon material to 1120 m²g⁻¹ for RCoAU composite.

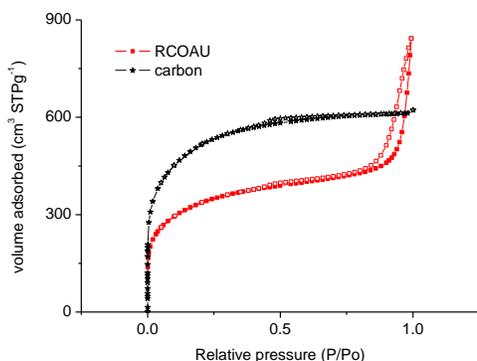


Fig. 2 Nitrogen adsorption isotherms for carbon material and composite RCoAU.

The structure evaluated by XRD proved the formation of crystalline LDH. The pattern of as prepared composite is well matched to the reported data for the compound $\text{Co}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot\text{H}_2\text{O}$ (JCPDS:51-0045). During calcinations, the characteristics peaks of LDHs gradually disappeared. Samples heated at 160 and 200°C became essentially amorphous. As the heating temperature was raised further, the crystallinity increased and the XRD patterns of the samples calcined at higher temperatures exhibited the characteristic peaks of both Co_3O_4 and CoAl_2O_4 .

Electrochemical properties of synthesized composites have been evaluated in two- and three-electrode systems. Among all synthesized composites, that obtained at 300°C exhibited the best properties. Two-electrode cells built from the composite pellets show the typical electrochemical characteristics of a capacitor. The voltammograms (Fig.3) have nearly rectangular shape, which indicates a quick dynamic of charge propagation for this kind of composite. The shape remains almost the same, indicating only the slight decrease in capacitance, even at higher scan rates.

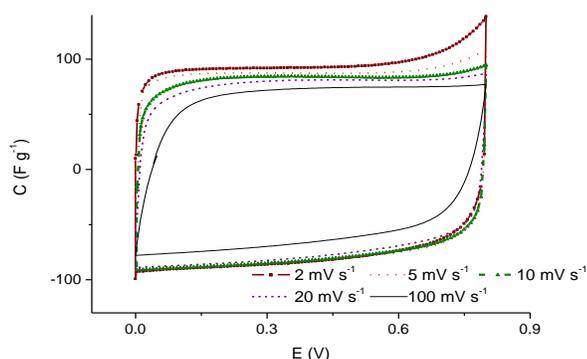


Fig. 3 Cyclic voltammograms for the RCoAU300 electrode at different scan rates in 6 mol L^{-1} KOH solution.

The specific capacitance has been evaluated from galvanostatic charge/discharge measurements. The

influence of constant current density on capacitance for carbon material and RCoAU composite is presented in Fig.4. It is worth noting, that the decrease is much smaller for composite comparing to the pure carbon material. The carbon electrode is able to work at constant current of 1 A g^{-1} while RCoAU300 maintains capacitance up to 5 A g^{-1} .

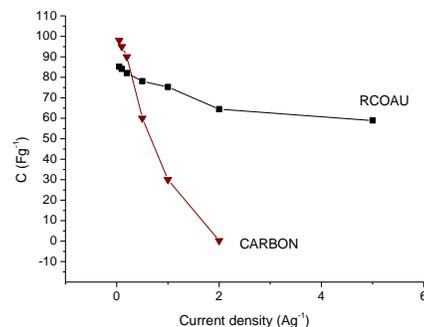


Fig. 4 Influence of constant current density on capacitance for carbon material and RCoAU composite.

Another advantage of this new type of electrode is its long term life. 15% loss of the capacitance has been observed after 15000 cycles at 1 A g^{-1} .

Conclusions

In the present study for the first time LDHs have been used as a source of metal oxide for reversible faradaic reactions in composite with activated carbon. Synergetic effect of the conducting carbon framework and the redox properties of the LDH may explain the improved electrochemical performance of the composite comparing to the pure activated carbon. High surface area of LDH/carbon composite and additional porosity which arises between particles can be accessible to the electrolyte in a mesoporous network. The carbon framework also improves the conductivity of the material, which is a key factor for obtaining materials possessing good electrochemical properties.

References

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