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Accepted Manuscript

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PII: S1385-8947(14)00643-3
DOI: http://dx.doi.org/10.1016/j.cej.2014.05.068
Reference: CEJ 12162

To appear in: Chemical Engineering Journal

Received Date: 28 February 2014
Revised Date: 2 May 2014
Accepted Date: 7 May 2014

Please cite this article as: B. Senthilkumar, M. Danielle, R. Kalai Selvan, M. Manickam, Facile and large scale combustion synthesis of α-CoMoO₄: mimics the redox behavior of a battery in aqueous hybrid device, Chemical Engineering Journal (2014), doi: http://dx.doi.org/10.1016/j.cej.2014.05.068

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Facile and large scale combustion synthesis of $\alpha$-CoMoO$_4$: mimics the redox behavior of a battery in aqueous hybrid device

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Abstract

We have made an investigation on cobalt molybdate ($\alpha$-CoMoO$_4$) as cathode material for aqueous hybrid system, in which the $\alpha$-CoMoO$_4$ positive material was prepared by a facile and scalable unique solution combustion synthesis (SCS) technique in air at ambient atmosphere. The $\alpha$-CoMoO$_4$ is stable at ambient temperature. The structural, morphological and pseudocapacitive properties of the $\alpha$-CoMoO$_4$ were studied by XRD, Raman, SEM and cyclic voltammetry. The XRD and Raman analysis evidenced the formation of pure crystalline $\alpha$-CoMoO$_4$ phase. The material $\alpha$-CoMoO$_4$ is reproducible using the simple combustion technique and the process scalability has been determined. The asymmetric hybrid device (AC vs. $\alpha$-CoMoO$_4$) (activated carbon denoted AC) exhibited good electrochemical performance in terms of specific capacitance (105 Fg$^{-1}$) and energy density (14.5 Wh Kg$^{-1}$). The asymmetric device shows very good cycling stability, with 98 % of initial capacitance retained after 4000 cycles. The $\alpha$-CoMoO$_4$ closely mimics the redox mechanism that contributes to the obtained specific capacitance.

Keywords: cobalt molybdate; activated carbon; aqueous; supercapacitor; combustion.

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1. Introduction

In recent years, transition metal molybdates (MMoO₄, M = Mn, Co, Ni, Cu and Fe) have attracted interest in the field of energy storage devices, such as Li-ion batteries [1-2] and supercapacitors [3-8]. This interest is primarily due to the electrochemical properties of the active metal ions in the chemically stable molybate structure, and the pseudocapacitive and semiconducting nature of the material [1-8]. Recently, Mai et al. [3] synthesized MnMoO₄/CoMoO₄ heterostructured nanowires by a micro-emulsion method and tested these materials as potential electrodes for supercapacitors. The MnMoO₄/CoMoO₄ electrode provided a promising specific capacitance (SC) of 200 Fg⁻¹ at a current density of 0.5 Ag⁻¹ and, of the electrodes tested, exhibited the best cycling stability [3]. Another recent work on CoMoO₄/MWCNTs nanoplatelets by Xu et al. [4] demonstrated a capacitance of 170 Fg⁻¹ at a current density of 0.1 Ag⁻¹. Liu et al. [5] reported a higher specific capacitance (326 Fg⁻¹ at 5 mA cm⁻²) for CoMoO₄.0.9H₂O nanorods synthesized by a hydrothermal process, with 96 % of initial capacitance remaining after 1000 cycles. In one of our recent works, combustion synthesized nano-sized α–NiMoO₄ showed high specific capacitance (425 Fg⁻¹ at 5 mA cm⁻²) with good cycling stability [6]. Overall, these studies illustrate the prominence and potential application of using molybdate for supercapacitors, but all the above mentioned studies on cobalt molybdates are prepared as composites and their reported synthetic methods are expensive and require stringent conditions. Clearly, a method that can produce large scale submicron sized CoMoO₄ structure with a use in energy storage of enhanced cyclability is of particular significance. To our best knowledge there is no work published on the CoMoO₄ synthesized via a facile and scalable chemical (combustion) synthesis route. The non-ceramic approach to the synthesis of cobalt molybdate is expected to produce materials with improved storage capacity that can be used as electrodes in capacitor applications. A key point of this work is to yield the final product (cobalt molybdate) with relatively short processing time at
moderate temperature having mono-dispersed particles which contribute to good electrochemical performance [9-10]. In this work, a simple solution combustion synthetic (SCS) technology is reported, the process make use of exothermic reaction occurred between the mixtures such as metal nitrates (as oxidizers) and urea (as fuel) [11]. This single step approach facilitated the reduction of particle size compared to the agglomerated morphology formed using conventional solid state (ceramic) synthesis. The asymmetric cell comprising $\alpha$-CoMoO$_4$ as cathode synthesized via a simple solution combustion route as reported in this work is a prerequisite for ongoing development and optimisation for practical applications.

Commercial supercapacitors are the combination of two symmetric activated carbon (AC) electrodes, and are of the electrical double layer capacitor (EDLC) type. These capacitors exhibit poor energy density (5-6 Wh kg$^{-1}$), due to charge storage being fully dependent on the electrical double layer [12]. Asymmetric capacitors with improved electrochemical performance have been fabricated by using a combination of EDLC and pseudocapacitive type electrodes [12-15]. There are several reports of asymmetric supercapacitors based on an AC negative electrode and a metal oxide as the positive electrode [13-16]. Recently, Lang et al. demonstrated a high specific capacitance (127 Fg$^{-1}$) and energy density (42 Wh kg$^{-1}$) for an AC||$\alpha$-Ni(OH)$_2$ cell [13]. Tang et al. reported an asymmetric cell based on AC||Ni-Co oxide showing a specific capacitance of 37 Fg$^{-1}$ at a high current density of 20 mA cm$^{-2}$ [14]. An interesting report shows excellent cycling stability for the cell based on AC||NaMnO$_2$, with only 3 % capacitance fading after 10000 cycles [15].

These reports motivated us to fabricate a full hybrid device comprising AC||CoMoO$_4$. To our best knowledge, this is the first time an asymmetric AC||$\alpha$-CoMoO$_4$ full cell has been built in an aqueous system, in which a unique combustion synthesis is employed. In view of the promising outcomes of our aqueous battery systems [17-18] using LiOH(aq) as
electrolyte, we have adopted a similar approach to this study. Aqueous systems are a preferable electrolyte choice for a number of reasons. They are far less expensive than organic solvents and have fewer disposal and safety issues. The ionic conductivity of LiOH(aq) is two orders of magnitude greater than that of organic electrolytes, allowing higher discharge rates and lower voltage drops due to electrolyte impedance. Hence, a solution of 2 M LiOH(aq) was used as an electrolyte in the current asymmetric capacitor study. The novel full cell (AC|α-CoMoO₄) discussed here provides nominal energy density of 14.5 Wh Kg⁻¹ while exhibiting excellent cycling stability up to 4000 cycles. The combustion synthesized cobalt molybdate mimics the redox (electron transfer) reactions of a battery that contribute to the achieved energy density. The term capacitor, device, and cell have been used interchangeably throughout this report.

2. Experimental

α-CoMoO₄ particles were synthesized by a solution combustion synthesis (SCS) technique using analytically pure Co(NO₃)₂.6H₂O (6.648 g), (NH₄)₆Mo₇O₂₄.4H₂O (4.033 g) and CO(NH₂)₂ (1.699 g) as fuel in 20 mL of deionised water. An oxidant-to-fuel ratio of 1:1 was maintained. The pH of the precursor solution was adjusted to 8 by dropwise addition of ammonia solution. The synthesis procedure followed was as for α-MnMoO₄ given in our previous work [19]. The as-prepared material was calcined at 400 °C to obtain the final product α-CoMoO₄.

Powder X-ray diffractometer 5635 (Siemens D500) with Cu-Kα radiation was used to identify the crystal structure. To investigate the morphology of the prepared sample, scanning electron microscopy (Philips Analytical XL series 20) was used. Cyclic voltammetry of the samples were carried out using an EG&G Princeton Applied Research Versa Stat III model. To prepare active electrode material, CoMoO₄ (85 wt %), carbon black (10 wt %) and
polyvinilidene fluoride (PVDF) (5 wt %) were suspended in 0.4 mL of N-methyl-2-pyrrolidinone (NMP) to form a slurry. An aliquot (10 µL) of slurry was coated on graphite sheet (area of coating: 1 cm²) to give a total mass of the electrode material of 1.25 mg. A solution of 2 M LiOH(aq) was used as electrolyte. For the three electrode tests a platinum wire electrode and a saturated Hg/HgO electrode were used as counter and reference electrode, respectively. The asymmetric cell was constructed using activated carbon (AC) coated on graphite sheet (area of coating: 1 cm²) and CoMoO₄ active electrode. The electrodes were separated by a polypropylene separator. The mass of the active electrode materials (AC and CoMoO₄) was 1.25 mg each, thus totalling 2.5 mg. The mass of the material was intentionally kept low in order to achieve quick cyclability. Activated carbon powder was used as-received from Chem Supply. Galvanostatic charge/discharge cycles of the cell were performed using an 8 channel battery analyzer from MTI Corp., USA, operated employing a battery testing method with the appropriate cut-off voltage.

3. Results and Discussion

Figure 1 (a) shows the XRD pattern of the CoMoO₄ sample synthesised via a facile combustion route. The observed diffraction peaks are in good agreement with the standard α-CoMoO₄ (JCPDS 025-1434). The diffraction peaks of as-prepared (before heating) CoMoO₄ (figure not given) were well matched with the standard CoMoO₄.xH₂O (JCPDS 026-0477) [6]. Note that it is well known that metal molybdates easily form hydrates when prepared by wet chemical synthesis [5, 20, 21] but when the precursor is heated at an elevated temperature 400 °C, α-CoMoO₄ has been formed without any traces of hydrates [22]. The calculated lattice parameters a = 9.628 Å, b = 8.865 Å, c = 7.694 Å, β = 112.62 and cell volume = 606.19 Å³ for the heated α-CoMoO₄ sample match well with the JCPDS (025-1434), confirming the formation of pure monoclinic α-CoMoO₄, C2/m space group.
Although CoMoO₄ crystallizes in two different forms such as α – and β – CoMoO₄ polymorphs but only α phase is stable at ambient temperature [23]. The phase β occurs on heating α – CoMoO₄ over 700° C [24]. Hence, we have obtained α-CoMoO₄ phase. Figure 1b shows the Raman spectrum of the α-CoMoO₄ sample. The bands observed at 267, 698, 810, 883 and 938 cm⁻¹ are typical of α-CoMoO₄ [25–26]. The absence of impurities, such as MoO₃ (which would produce a band at 996 cm⁻¹), further substantiates the XRD analysis [25–26] of the synthesized product as pure phase α-CoMoO₄. The SEM image (Figure 1c) shows granular α-CoMoO₄ particles with a uniform size distribution in the range 1-5 µm. The material characteristics of α-CoMoO₄ are primarily governed by nature of the fuel used and oxidant-to-fuel ratio [19] which is an attractive feature of combustion route. Hence, the chosen combustion technology is simple and practical approach for scaling up and commercialisation.

Figure 2 (a–b) gives the cyclic voltammograms (CVs) of α-CoMoO₄ in a three electrode cell. To evaluate the effect of scan rate, CV curves (Fig. 2a) were recorded over a potential range from 0.1 to 0.6 V vs. Hg/HgO at a various scan rate of 1 to 20 mVs⁻¹. An oxidation/reduction peak can be observed, suggesting that the capacitance of the material is due in part to pseudocapacitance. The redox peak observed at the potentials (A₁ = 0.36 V; C₁ = 0.30 V) are due to the following faradic redox reactions (Eq. 1 and 2) having the charge-transfer kinetics of Co²⁺/³⁺ in the metal molybdate framework, identified from the Pourbaix diagram of cobalt and presented in recent works based on CoMoO₄ [3-5]

\[
3[\text{Co(OH)}_3]^- \leftrightarrow \text{Co}_3\text{O}_4 + 4\text{H}_2\text{O} + \text{OH}^- + 2\text{e}^- \quad \text{Eq. [1]}
\]

\[
\text{Co}_3\text{O}_4 + \text{H}_2\text{O} + \text{OH}^- \leftrightarrow 3\text{CoOOH} + \text{e}^- \quad \text{Eq. [2]}
\]

When α-CoMoO₄ is introduced in the strong base electrolyte (2 M LiOH aq.) with a pH of over ≥ 8.0, cobalt hydroxide (Co(OH)₃) is precipitated in aqueous electrolyte solution
During the cyclic voltammetric measurements, while varying the applied potential, (Co(OH)$_3$) is oxidised to CoOOH at the potential ~0.35 V vs. Hg/HgO. The capacitance contribution is based on the process of adsorption/desorption of electrolyte anions (OH$^-$) and the fast redox reactions at the surface of the active material [3–5]. The OH$^-$ ions are unequivocally contributed from the aqueous electrolyte, as the synthesized cobalt molybdate $\alpha$-CoMoO$_4$ showed no traces of hydrates (as evidenced from XRD, Fig. 1a). The anodic and cathodic peaks shift towards positive and negative potentials respectively, and the height of the peak current varies, as the scan rate is increased. This indicates that at a lower scan rate, the entire surface of the working CoMoO$_4$ electrode was fully electroactive, while redox processes become the rate determining step at increased scan rates. The kinetics of the interfacial redox reactions and the rates of electronic and ionic transport are sufficiently rapid at the scan rate of 5 mVs$^{-1}$, as confirmed by the increase in peak current with scan rate [3–5].

Figure 2b shows the effect of applied potential on multiple cycling. While electrodes are reversible in both cases (narrow and wide potential region), capacitance fading, as evidenced by variation in redox peak currents, is observed only for the wide voltage region. This is perhaps due to surface passivation and structural transformation of the material. On the basis of this study, a scan rate of 5 mVs$^{-1}$ within a potential range of 0.1 and 0.6 V were selected for further single electrode studies. A continuous cycling test (100 cycles) of the CoMoO$_4$ electrode revealed that peak potential and current response were identical as in Fig. 2b. The galvanostatic cycling performance of the CoMoO$_4$ electrode between 0.1 and 0.7 V at a current density of 5 mA cm$^{-2}$ is shown in fig. 2c. The charge-discharge characteristics of the CoMoO$_4$, as exhibited by the sloping profile and slight curve occurring at the higher voltage region (0.6 vs Hg/HgO) may be attributed to the pseudo capacitance, possibly resulting from fast redox reactions (Eq. 1–2). The active materials showed an excellent cycling stability in the applied potential window.
Activated carbon (AC) with a high surface area (1700 m²/g) is used to increase the energy density of the asymmetric capacitors. To evaluate the capacitive characteristics of the activated carbon, cyclic voltamogram and galvanostatic charge-discharge cycles were performed. Figure 3a shows the CV obtained at a scan rate of 5 mVs⁻¹. Clearly no redox peaks were observed in the voltammograms. This supports formation of the electric double layer (EDL) through electrostatic interaction and ion adsorption on the carbon surface, rather than faradaic reaction [27]. The typical EDL characteristic shape of the cyclic voltammogram seen in Fig. 3a is found to be stable on long term cycling. The constant current charge-discharge test was carried out between 0 and −1.0 V at a current density 5 mA cm⁻² to investigate the electrochemical performance of the AC electrode (Fig. 3b). The identical symmetric curves showed a larger specific area, as used in this study, contributes to energy storage through the double layer mechanism [28] and the material is found to be highly reversible after 25 cycles.

Figure 4 (a) shows the cyclic voltammogram of an assembled asymmetric hybrid capacitor coupled with two dissimilar electrodes (AC||CoMoO₄). The voltammogram was recorded at scan rates of 5 and 10 mV s⁻¹. The observed redox peaks mimics pseudocapacitive-type charge storage in the cell as normally observed for battery electrochemistry. Li adsorption/desorption may be possible at the anode (AC), and the formation of the electrical double layer leads to the charge storage. The surface redox reactions due to the electrolyte anions (OH⁻) are at the positive electrode; this produces the quasi-rectangular CV curves. The possible electrochemical reactions in the cell are, for the positive electrode, those shown in Eq. 1-2, and for the negative electrode, as given below [3, 5, 28].

Negative electrode

\[
\text{AC} + x \text{Li}^+ + xe^- \leftrightarrow \text{AC (xe⁻)} || x\text{Li}^+ \text{ (|| indicates double layer)} \quad \text{Eq. [3]}
\]
The galvanostatic charge-discharge cycles were performed at various current densities for the asymmetric cell, as given in Figure 4b. A quasi-symmetric profile, further supporting pseudocapacitive behaviour, is evident. A small IR drop was observed in the charge/discharge profile due to the equivalent series resistance (ESR) of the cell. The specific capacitance (SC), energy density (E) and power density (P) of the full cell were calculated using the following equations:

\[ C = \frac{I \Delta t}{m \Delta V} \]  
Eq. [4]

\[ E = \frac{1}{2} C (\Delta V)^2 \]  
Eq. [5]

\[ P = \frac{I \Delta V}{2m} \]  
Eq. [6]

where I is the current, m is total mass of the active material of the two electrodes, and \( \Delta t \) is the discharge time corresponding to the voltage window, \( \Delta V \). The specific capacitance (SC) value obtained for the cell from Figure 4b is 105, 98, 96, 93 and 90 F/g at current densities 1, 2, 3, 4 and 5 mA/cm\(^2\) (0.4, 0.8, 1.2, 1.6 and 2 A/g), respectively. After an increase to the current density 5 mA/cm\(^2\), 86 % of the SC remains, demonstrating high rate capability of the cell.

A ragone plot for the cell is shown in Figure 4c. The asymmetric hybrid capacitor delivers an energy density of 14.5 Wh kg\(^{-1}\) at a power density of 200 W kg\(^{-1}\) and 12.5 Wh kg\(^{-1}\) even at a high power density of 1000 W kg\(^{-1}\). Note that these energy and power density values refer to the mass of active materials only; the limitations of reporting these values in this way [29] should be borne in mind. Nevertheless, these cell capacitance and energy density values are significantly greater than the reported values for the AC||Ni-Co oxide [14], AC||Al-Co oxide [16], AC||Ni\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)(OH)\(_2\) [30], AC||Fe\(_3\)O\(_4\) [29] and AC||MnO\(_2\) [31] asymmetric capacitors with identical experimental conditions to those employed here.

The cycle life of the device was investigated up to 4000 cycles. Figure 4 (d) shows the stability of the SC and coulombic efficiency of the cell obtained at 5 mA/cm\(^2\) tested for 4000
charge-discharge cycles. A high coulombic efficiency (> 95%) was observed for the asymmetric hybrid (AC/CoMoO$_4$) cell, and 95% of initial capacitance was retained even after 4000 cycles. The discharge specific capacitance of the hybrid capacitor investigated in this study decreased with an increase in current rate (density) from 1 to 5 mA cm$^{-2}$ (Fig. 5) illustrating the decrease in utilization of the CoMoO$_4$ material. Nevertheless, the hybrid capacitor sustained to high current rate and the efficiency of the cell is still high at 95% for 5 mA cm$^2$.

4. Conclusions

In the present work, $\alpha$-CoMoO$_4$ cathode material was successfully synthesized by the solution combustion technique. The combustion route is very simple, environmentally friendly and reproducible while less expensive as it doesn’t require any expensive reagents and found suitable for scalable synthesis. For the first time, a novel asymmetric AC$||$CoMoO$_4$ hybrid device was fabricated using 2M LiOH(aq) electrolyte. The asymmetric device exhibited very good electrochemical performance: high specific capacitance (105 Fg$^{-1}$) and energy density (14.5 Wh Kg$^{-1}$) attributed to both EDLC and pseudocapacitance mechanisms. The fabricated device showed good cycling stability up to 4000 cycles compared to other asymmetric capacitors. Hence the aqueous cell may be potentially applied to practical applications, including electric vehicles, UPS devices, cell phones and computer notebooks. The cell performance may be further enhanced by employing an alternative negative electrode with a high working potential.

Acknowledgements

The author (M. M) wishes to acknowledge the funding bodies, Australia-India Strategic Research Fund (AISRF) for providing an early-career research fellowship and Australian
Research Council (ARC). This research was supported under ARC’s Discovery Projects funding scheme (DP1092543). The views expressed herein are those of the authors and are not necessarily those of the Australian Research Council.

References


Figure 1 (a) XRD pattern, (b) Raman spectrum, (c) SEM image of combustion synthesized $\alpha$-CoMoO$_4$. 
Figure 2 (a) Cyclic voltammogram at a various scan rates (b) at a different voltage region and (c) charge-discharge profiles at a current density of 5 mA cm$^{-2}$ of $\alpha$-CoMoO$_4$. 
Figure 3 (a) Cyclic voltammogram at a scan rate of 5 mVs⁻¹ and (b) Galvanostatic charge-discharge profiles at a current density of 5 mA cm⁻² of activated carbon (AC) electrode.
Figure 4 (a) Cyclic voltammogram profiles of AC∥α-CoMoO$_4$ asymmetric hybrid capacitor at scan rates of 5 and 10 mVs$^{-1}$, (b) Galvanostatic charge-discharge curves of the asymmetric capacitor at a various current densities, (c) Ragone plot of the asymmetric capacitor and (d) Cycling and efficiency performance of the capacitor at a current density of 5 mAcm$^{-2}$. 
Figure 5 The specific capacitance of AC||α-CoMoO₄ asymmetric hybrid capacitor as a function of current rate. Bar graph illustrates the charge and discharge capacitance and its efficiency.
**Highlights**

- A cobalt molybdate based asymmetric hybrid device has been fabricated.
- Facile and large scale combustion synthesis of $\alpha$-CoMoO$_4$ is demonstrated.
- Specific capacitance of 105 F/g is obtained in aqueous electrolyte.
- The extracted energy density of the system is 14.5 Wh/Kg.