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Tunable Supercapacitor Performances of Potentiodynamically Deposited Urea-doped Cobalt Hydroxide

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Abstract

Cobalt hydroxide with or without added urea content was potentiodynamically synthesized from nitrate bath and the resultant hydroxides were examined as electrode material for supercapacitor applications. The deposited hydroxides were characterized by X-ray diffraction, field-emission scanning electron microscope and Fourier transformed infra-red spectroscopy. By having urea in the nitrate bath, the specific capacitance of $Co(OH)_2$ could be tuned from 700 Fg^{-1} to 1200 Fg^{-1} at a current of 0.5 mA. It was shown that the addition of just 2 wt.% urea in the nitrate bath had strong influence on the supercapacitor performances, exhibiting the highest specific capacitance of 1200 Fg^{-1}. The high-performances of the urea-doped $Co(OH)_2$ were attributed to better access of electrolyte due to well stabilized basal length.

Keywords: Energy storage; Supercapacitors; Cobalt hydroxide; Electrodeposition

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1. Introduction

Supercapacitors have recently attracted for meeting the required energy demands of various consumer electronics including mobile phones, digital cameras, laptops, etc. The ability of supercapacitors to store passable energy and release it in a high rate (high power) for long cycle life, is a significant improvement to substantiate the batteries and other energy storage devices. It is accepted that on the basis of charge-storage mechanisms, the electrochemical capacitors are classified into two types, viz., electrochemical double-layer capacitors (EDLCs) and pseudocapacitors. In EDLC, charges are stored in the form of electrical double-layer and has low specific capacitance, as their charge storage is mainly limited by the available active surface area, while in pseudocapacitors, charges are stored due to fast electrosorption/ electrodesorption or redox processes taking place at or near the electrode/electrolyte interface and have large specific capacitance.[1,2] Due to large specific capacitance exhibited by pseudocapacitors, significant progress has been made recently for efficient electrode materials. For example, ruthenium oxide exhibited a specific capacitance of 720 Fg^{-1} and stimulated the initial interests in this class of materials.[3] However, due to high cost of the ruthenium, research interests have been currently focused on other inexpensive electrode materials with similar or even better performances. In this regard, conducting polymers,[4,5] transition-metal oxides,[6,7] hydroxides,[8,9] and composites[10,11] are being investigated.

Among the various transition-metal hydroxides those were examined as electrode for supercapacitors, cobalt hydroxide has received a much attention quite recently, because of its attractive electrochemical properties.[12,13] The hydroxides of cobalt exist in two polymorphic forms known as α- and β-$Co(OH)_2$. The brucite-like β-$Co(OH)_2$ has a hexagonal packing of hydroxyl ions with Co^{2+} ions occupying alternate rows of octahedral sites, while the α-$Co(OH)_2$ is reported to be isostructural with hydrotalcite-like compounds that consist of positively charged $Co(OH)_{2-x}$ layers with interlayer spacings of about 7 Å and the charge is balanced by anions (eg., NO_3^-, CO_3^{2-}, Cl^-, etc.) present in the interlayer space.[14]

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As an electrode material for supercapacitor application, Hu *et al*., have reported a specific capacitance of about 410 Fg^{-1} for sheet-like morphology of $Co(OH)_2$.[15] Yuan *et al*., have achieved a specific capacitance of 430 Fg^{-1} for mesoporous $Co(OH)_2$ at a current density of 10 mA cm^{-2}.[16] Preparation method had strong influence on the supercapacitor performances of cobalt hydroxide. A few successful methods such as microwave irradiation,[17] solvothermal,[18] co-precipitation,[19] and electrodeposition[20] have been adopted for synthesis of $Co(OH)_2$. Among them, electrodeposition is the simple and inexpensive synthetic route to obtain $Co(OH)_2$. For example, Gupta *et al*., have performed potentiostatic deposition of $Co(OH)_2$ and reported a specific capacitance of about 840 Fg^{-1}.[20] Kong *et al*., have carried out deposition of $Co(OH)_2$ on nickel foil/foam from nitrate bath, and investigated the effects of electrodeposition time and applied potential on the capacitance of α-$Co(OH)_2$ thin films.[21] They showed that the film deposited on nickel foam at -1.0 V vs. SCE had better electrochemical properties due to better access of electrolyte to the electrode material.

Substitution of transition-metal ion or non-transition metal ion lead to formation of double hydroxides or layered double hydroxides (LDHs). These LDHs exhibited improved supercapacitor performances. The improved performances were attributed to wider operating potential window associated with LDHs.[22] It is reported that in the interlayers of $Co(OH)_2$ different anions or neutral molecules can be accommodated. Having anions or neutral molecules at the interlayer resulted in increased basal length as reported by Yarger *et al.* For example, the addition of surfactant molecule, sodium dodecyl sulphate during deposition of $Co(OH)_2$ resulted in the increased basal length from 7 to 31 Å.[23] To the best of our knowledge, reports on the influence of the basal length of $Co(OH)_2$ on the supercapacitor performances are scanty. Thus, in the present work, urea was intentionally added to the nitrate bath to synthesize urea-doped $Co(OH)_2$ with enhanced basal length. Then, the effects of urea addition during the electrodeposition of $Co(OH)_2$ was examined and the obtained samples were utilized as electrode material for supercapacitor applications. As a result, it

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turned out that 2 wt.% urea-added $Co(OH)_2$ exhibited excellent specific capacitance of as high as 1200 Fg^{-1}, while the pure $Co(OH)_2$ exhibited the specific capacitance of only about 700 Fg^{-1}. The detailed investigations of tunable supercapacitor performances of $Co(OH)_2$ with the influence of urea addition are reported here.

2. Experimental

Analytical grade $Co(NO_3)_2{\cdot}6H_2O$ (Fisher Scientific), urea (Loba Chemie) and KOH (Fisher Scientific) were used without further purification. The 304 grade stainless-steel having 0.4 mm thickness was purchased from a local shop. The stainless-steel (SS) was cut into stripes of 10 x 0.5 cm and polished with emery paper to have a rough finish then washed with ethanol and distilled water before being dried in an oven. The exposed area was 0.5 x 0.5 cm, the rest of area was masked with the teflon tape leaving provision for current collector. A three-electrode cell was assembled for all the electrochemical experiments. The cell consisted of a platinum wire (area: 3.2 cm^{-2}) as counter electrode, an Ag/AgCl (saturated KCl solution) as reference electrode, and the above mentioned SS as working electrode. The 0.2 M $Co(NO_3)_2$ solution was prepared in the distilled water. The 0.2 M $Co(NO_3)_2$ solutions containing each of 1, 2, 4, 6, 8 and 10 wt.% urea were also prepared in distilled water separately. The potential window for potentiodynamic deposition was set from 0 to −1.4 V vs. Ag/AgCl. The deposition was done at the scan rate of 200 mV s^{-1} for the required no. of cycles. Both sides of the SS were deposited with cobalt hydroxide. The resulting films were then carefully washed with distilled water and dried in air at 60 °C for overnight. The weights of the deposits were measured by means of electronic balance (Shimadzu, AW 320) and were around 0.5 mg.

The crystal structure of the deposited $Co(OH)_2$ was examined by using X-ray diffractometer (PANalytical PW3040 Cu Kα 1.5406 Å). The infra-red spectrum of hydroxide deposits scraped from the SS electrode was recorded by using a Fourier transformed infra-red (FT-IR) spectrometer (Thermo Nicolet 6700). The surface morphology of all the deposits was

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investigated by field-emission scanning electron microscope (FE-SEM) (FEI Quanta FEG 200). All the electrochemical depositions and characterizations of cobalt hydroxide were performed with an Autolab electrochemical workstation (Eco Chemie, PGSTAT 302N). The cyclic voltammetric and galvanostatic charge-discharge studies were carried out in a three-electrode electrochemical cell containing 1M KOH electrolyte. The cyclic voltammogram (CV) was recorded in a potential range of -0.1 and 0.45 V vs. Ag/AgCl at various scan rates (5, 10, 20, 50, 80, and 100 mV s^{-1}). The galvanostatic charge-discharge tests were carried out at currents of 0.5, 1, 2, 3 and 5 mA in a potential range of 0 to 0.45 V. The cycle life test for pure $Co(OH)_2$ and 2 wt.% urea-doped $Co(OH)_2$ was done at a current of 5 mA for 1000 cycles.

3. Results and Discussion

3.1 Hydroxide formation

Soon after starting the deposition, a clear change in the color of the SS surfaces was observed. Within a few cycles, the silvery colour of the SS surface turned to the greenish blue, indicating deposition of cobalt hydroxide. The deposition cobalt hydroxide on the SS surface can be expressed by the following reactions.[24]

$$NO_3^- + 7H_2O + 8e^- \rightarrow NH_4^+ + 10OH^- \qquad (1)$$

$$Co^{2+} + 2OH^- \rightarrow Co(OH)_2 \qquad (2)$$

The nitrate ion undergoes reduction to form NH_3, which on protonation results in the formation of NH_4^+, leading to increase in the local pH at electrode/ electrolyte interface. The increased local pH results in the deposition of $Co(OH)_2$ on the SS. It was observed that the addition of urea did not affect the deposition. The decomposition potential of urea is 1.7 V vs. Ag/AgCl.[25] This potential is away from the above mentioned deposition potential-range. Thus, urea is stable in the depositing medium.

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3.2 Structural and morphological characterizations

Figure 1 shows the XRD patterns of the pure and each of the urea-doped $Co(OH)_2$ samples deposited on the SS substrate. The XRD pattern consists of Bragg peaks at angles 10.05°, 14.09°, 17.3°, 20.12°, 33.46° and 59.30°. These set of Bragg peaks can be conveniently indexed to α-$Co(OH)_2$ according to the standard XRD pattern of the JCPDS file, PDF # 46-0605. Almost similar XRD pattern was reported to $Co(OH)_2$ synthesized by hydrothermal method.[25] It is noted that the interlayer space of about 7.0 Å was observed for pure $Co(OH)_2$. It can be seen that the above mentioned set of Bragg peaks were also present in all the urea-doped $Co(OH)_2$ samples. It is interesting to note that there is a gradual shift of Bragg peaks towards lower angle, as the urea content in the nitrate bath increased. This shift in Bragg peak position indicates that the urea present in the nitrate bath gone into the structure of $Co(OH)_2$ during its formation. The interlayer spacing of the urea-doped $Co(OH)_2$ was found to be about 9.0 Å, which is notably higher than that observed for pure $Co(OH)_2$. The peak position of first Bragg angle is taken as interlayer space.[23] The peaks at Bragg angles, 33.40° and 69.50° are evidence for the presence of turbostratic nature of α-$Co(OH)_2$.

The FT-IR spectrum of the deposited $Co(OH)_2$ from the nitrate bath without or with each of different urea contents is given in Fig. 2. It is noted that in all case intense broad band is seen in the frequency range of 3600-3000 cm^{-1} which is ascribed to hydrogen-bonded OH arising from hydroxyl groups of cobalt hydroxide and the interlayer water molecules. The absence of sharp peak in this region confirms that there is no free -OH group which in turn confirm that the formed cobalt hydroxide is α-phase. The peak around 1380 cm^{-1} is characteristic peak of intercalated nitrate ions. The peak at 670 is assigned to Co-O, as reported elsewhere.[19] It is noted that the peak in the range of 3600-3000 cm^{-1} observed for pure $Co(OH)_2$ is symmetric, while that for the urea-doped $Co(OH)_2$ samples is asymmetric. As the urea content in the nitrate bath is increased, this peak is becoming highly asymmetric and broader. Such a peak shape may be considered for the presence of $-NH_2$ group which might have come from the added urea. The peak at 1630 cm^{-1} is due to the presence of C=O

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vibration again could have come from urea. The appearance of bands at 1440 cm^{-1} and 1160 cm^{-1} confirm the presence of C-N bond of the urea. The presence of these peaks are well pronounced in all the urea-added samples, especially at higher urea contents. Thus, IR data confirm that the cobalt hydroxides are in the hydrous form with plenty of water, NO_3^- and the added urea in the interlayers.

It is well known that cobalt hydroxide exists in two different forms, known as α and β forms. While the colour of the β-$Co(OH)_2$ is pink and that of the α-$Co(OH)_2$ is green. It was observed that the deposited pure $Co(OH)_2$ sample was green in colour. The greenish colour of the $Co(OH)_2$ changed to bluish as the urea content in the nitrate bath increased. Jeevanandam *et al.*, has reported the change of green colour to blue for $Co(OH)_2$ prepared by ultrasonication.[14] Thus, based on the XRD, IR data and the appearance of $Co(OH)_2$ colour, it is confirmed that the deposited cobalt hydroxide is α-form with the urea in the interlayers, leading to the basal length of about 9 Å. The increased basal length is expected to influence on electrochemical activities. Figure 3 schematically shows the structure of $Co(OH)_2$ and the change of interlayer upon doping urea.

Figure 4 shows the FE-SEM images on the surface of the deposited $Co(OH)_2$ with or without urea in the nitrate bath. The morphology of the low urea-doped $Co(OH)_2$ deposits consisted of flakey structure with the average flakey thickness of about 60 nm and pore size of 200 nm. It is expected that these pores will also lead to better access of electrolyte ions and hence better electrochemical activities. It can be seen that at higher urea-doped $Co(OH)_2$, the electrode matrix looks denser with large flakey thickness (~ 90 nm). The dense matrix might hinder electrolyte access during electrochemical reactions.

3.3 Supercapacitor characterizations

The supercapacitor properties of each of the deposited-$Co(OH)_2$ electrodes were characterized by cyclic voltammetric and galvanostatic charge-discharge studies in 1 M KOH. Figure 5 shows the cyclic voltammograms (CVs) of the pure and each of the urea-

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doped $Co(OH)_2$ electrodes at a scan rate of 5 mV s^{-1} in the potential range of -0.1 to 0.45 V. All the deposits show a pair of strong redox peaks. The appearance of redox peak and non-rectangular shape of CV indicate that the capacitance characteristics are governed mainly by Faradaic reactions. For the pure $Co(OH)_2$, oxidation peak appears at 0.15 V and the reduction peak at 0.06 V with a peak potential separation of about 90 mV which is slightly higher value than that for a single electron transfer reaction (69 mV). The appearance of redox peak is attributed to the following electrochemical reaction.[21, 22]

$$Co(OH)_2 + OH^- \rightleftharpoons CoOOH + H_2O + e^- \quad (3)$$

It is noted that, at higher urea content (> 8 wt.%), the peak potentials are shifted to more negative. The common factors which may lead to shift in CV peaks are different reaction (other than eqn. (3)), iR drop (resistance offered by electrolytic solution), poor electrode kinetics and quasireversiblility.

It can be seen that the peak current increases with the increase of urea content, reaches a maximum then the lowest peak current is exhibited by the 10 wt.% urea-doped Co(OH)2 electrode. The specific capacitance can be calculated by using the following equation.

$$C = \frac{Q}{V \bullet m} \ Fg^{-1} \quad (4)$$

where, C is specific capacitance (Fg^{-1}), Q is average charge of electrode (Coulomb), V is potential window (V) and m is active mass of electrode material (g). It turned out that the obtained specific capacitances for each of pure $Co(OH)_2$, 2, 4, 6, 8 and 10 wt.% urea-doped $Co(OH)_2$ electrodes were about 560, 970, 820, 850, 500, and 150 Fg^{-1}, respectively. It can be seen that having urea in the interlayer of $Co(OH)_2$ resulted in the enhanced specific capacitance, especially if the urea content is between 2 and 6 wt.%. Among the various urea contents added, the highest specific capacitance is exhibited by just 2 wt.% addition. Thus, it is evident that the presence of urea in the interlayer $Co(OH)_2$ has strong influence on the charge storage.

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Galvanostatic charge-discharge studies were done for all the deposited samples at a current of 0.5 mA. The obtained CD curves are shown in Fig. 6 (a). It is seen that in all cases the CD curves are mirror images, showing charging and discharging process are highly reversible in nature. It is noteworthy that major contribution for capacitance comes from the potential range of 0 to 0.2 V which substantiates the CV results discussed above. Noted difference can be seen in the charging and discharging times for the urea-doped $Co(OH)_2$ samples, especially if the urea content is between 2 to 6 wt.%. The urea-doped $Co(OH)_2$ electrode showed significantly large charge-discharge times which indicate high charge storage. The specific capacitance can be calculated from the discharge curve according to the following relationship:

$$C = \frac{I \cdot t}{V \cdot m} \ Fg^{-1} \qquad (5)$$

where C is the specific capacitance (Fg^{-1}), I is discharge current (A), t is discharging time (s), V is the discharge potential and m is the active mass of electrode material (g). The obtained specific capacitances for each of the deposits are plotted against the urea content added in the nitrate bath and shown in Fig. 6 (b). It is seen that the specific capacitance of $Co(OH)_2$ can be tuned from 700 Fg^{-1} to as high as 1200 Fg^{-1}. Almost double the enhancement of specific capacitance could be achieved if just 2 wt.% urea is added to the nitrate bath. It is noteworthy that this is the highest specific capacitance value achieved so far in the literature for $Co(OH)_2$-based electrodes. It is also noted that if the urea content in the nitrate bath is between 1 to 6 wt.%, the specific capacitance of $Co(OH)_2$ can be improved largely. Such an observation is new and has not been reported so far. Addition of beyond 6 wt.% urea resulted in decreased specific capacitance. The specific capacitance of the pure $Co(OH)_2$ observed in the present work is about 700 Fg^{-1} which is significantly higher than that the value reported elsewhere.

Since the 2 wt.% urea-doped $Co(OH)_2$ electrode exhibited the highest specific capacitance, further supercapacitor characteristics were done on this electrode. For

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comparison, supercapacitor characteristics of pure $Co(OH)_2$ electrode were also done. Figure 7 shows the CVs recorded for the 2 wt.% urea-doped $Co(OH)_2$ in 1 M KOH at various scan rates. It is seen that in all scan rates, the electrode shows redox peak. The peak currents increased with increase of scan rate, as usually observed. The specific capacitance of the 2 wt.% urea-doped $Co(OH)_2$ estimated from CV curves of each of 5, 20, 50, 80, and 100 mVs^{-1} scan rates are about 900, 930, 850, 770, and 700 Fg^{-1}, respectively. As the scan rate increases, the specific capacitance decreases which is usually observed. Interestingly, it is noted that the 2 wt.% urea-doped $Co(OH)_2$ electrode showed a specific capacitance of 700 Fg^{-1} even at a high scan rate of 100 mVs^{-1} which is remarkable. This means that the 2 wt.% urea-doped $Co(OH)_2$ electrode has good rate capability which is one of the important aspects for practical supercapacitor device.

Figure 8 (a) shows the charge-discharge characteristics of the 2 wt.% urea-doped $Co(OH)_2$ electrode in the potential range of 0 - 0.45 V at various currents. In each case, the charge-discharge curves appear like mirror images, showing high reversibility. The specific capacitance values of the 2 wt.% urea-doped $Co(OH)_2$ at discharge currents of each of 0.5, 1, 2, 3 and 5 mA are 1260, 1220, 1170, 1130 and 1090 Fg^{-1}, respectively (Fig. 8 (b)). It is seen that these values are much higher than that observed for pure $Co(OH)_2$. It is noted that even at the high current of 5 mA, the SC value is as high as 1090 Fg^{-1}. This demonstrates excellent supercapacitor characteristics of the 2 wt.% urea-doped $Co(OH)_2$ electrode. All the experiments were conducted twice and the obtained results were within 2% variation.

The specific energy and specific power of the 2 wt.% urea-doped $Co(OH)_2$ electrodes were calculated from the following equations:

$$\text{Specific power} = \frac{I \bullet \Delta V}{m} \quad \text{W kg}^{-1} \tag{6}$$

$$\text{Specific energy} = \frac{I \bullet t \bullet \Delta V}{m} \quad \text{Wh kg}^{-1} \tag{7}$$

where I is the discharge current (A), t is the discharge time (s), ΔV is the discharge potential (V), and m is the active mass of electrode material (kg). The specific energy and specific

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power of the 2 wt.% urea-doped $Co(OH)_2$ electrodes were estimated and the obtained results are shown in Ragone plot (Fig. 9). The 2 wt.% urea-doped $Co(OH)_2$ electrode has remarkable specific energy of 70 Wh kg^{-1} at a high specific power of 450 W kg^{-1} which is much higher than that of the pure $Co(OH)_2$ electrode whose specific energy is only 40 Wh kg^{-1} at the specific power of 350 W kg^{-1}. Almost double the enhancement in specific energy could be achieved by just adding 2 wt.% urea in the nitrate bath. Noticeably, the retention of specific energy as the specific power increased is also remarkable. These results demonstrate that the urea-doped $Co(OH)_2$ electrode is a potential candidate for high performance supercapacitor materials.

To examine the stability of the electrode, the galvanostatic charge-discharge cycling was done for 1000 cycles at a current of 5 mA. The obtained results are shown in Fig. 10. For comparison, the data obtained for pure $Co(OH)_2$ were also presented. The 2 wt.% urea-doped $Co(OH)_2$ electrode retains its original specific capacitance as high as 80% even at 1000th CD cycle. It is noteworthy that the 2 wt.% urea-doped $Co(OH)_2$ exhibited about 900 Fg^{-1} even at 1000th CD cycle, while the pure $Co(OH)_2$ exhibited only about 490 Fg^{-1}. Thus, the present study demonstrates that having urea in the interlayer helped to achieve excellent specific capacitance as well as improved cycle life.

It is reported that in the interlayers of $Co(OH)_2$, anions such as CO_3^{2-}, NO_3^-, and some neutral molecules like H_2O are trapped during synthesis of $Co(OH)_2$. In the present work, urea was intentionally added in the nitrate bath that has resulted in trapping urea molecules in the interlayers of $Co(OH)_2$. As the urea content is increased more and more urea molecules are getting trapped in the interlayers which has resulted in increased basal length, as schematically shown in Fig. 3. The improved specific capacitance of the urea-doped $Co(OH)_2$ electrode could be due to better access of electrolyte during CV and CD studies as the interlayer distance is large. In addition, the large interlayer space seem to be well stabilized by the presence of urea molecules which has resulted in better cycle life with good retention of specific capacitance in the case of 2 wt.% urea-doped $Co(OH)_2$. It should be noted that

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urea molecules are held by strong hydrogen bond in the interlayers of $Co(OH)_2$. Thus, complete leach out will be difficult, although a small amount of urea may undergo leaching during electrochemical measurements in KOH. As it can be seen in SEM, the electrode. The low specific capacitance exhibited by higher urea-doped $Co(OH)_2$ electrodes (> 6 wt. %) could be due to poor access of electrolyte during electrochemical reaction, because of the denser electrode matrix, as confirmed by FE-SEM analysis. The influence of addition of other molecules such as poly ethylene glycol is under progress.

4. Conclusions

The α-phase of $Co(OH)_2$ was potentiodynamically deposited on SS substrate with the addition of different urea contents in the nitrate bath. All the deposited $Co(OH)_2$ electrodes showed redox peak indicating supercapacitor property. By having urea in the nitrate bath, the specific capacitance of the $Co(OH)_2$ electrode could be tuned from 700 Fg^{-1} to 1200 Fg^{-1}. The 2 wt.% urea-doped $Co(OH)_2$ electrode retains as high as 80% of its original specific capacitance even at 1000th CD cycle. Both the specific energy and the specific power can also be significantly enhanced by having urea in the interlayers of $Co(OH)_2$. The improved supercapacitor performances were attributed to better access of electrolyte due to enhanced as well as well stabilized basal length by having urea molecules in the $Co(OH)_2$ structure.

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References

1. B. E. Conway, Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications; Kluwer Academic/Plenum Press, New York, 1999.
2. G. Wang, L. Zhang and J. Zhang, Chem. Soc. Rev., 2012, **41**, 797-828.
3. I. H. Kim and K. B. Kim, Electrochem. Solid-State Lett., 2001, **4**, A62-A64.
4. C. A. Amarnath, J. H. Chang, D. Kim, R. S. Mane, S.-H. Han and D. Sohn, Mater. Chem. Phys., 2009, **113**, 14-17.
5. Y. E. Miao, W. Fan, D. Chen and T. Liu, ACS Appl. Mater. Interfaces, 2013, **5**, 4423-4428.
6. S. Devaraj and N. Munichandraiah, J. Solid State Electrochem., 2007, 12, 207-211.
7. J. Junyi, L. Zhang, H. Ji, Y. Li, X. Zhao, X. Bai, X. Fan, F. Zhang and R. Ruoff, ACS Nano, 2013, **7**, 6237-6243.
8. S. Yang, X. Wu, C. Chen, H. Dong, W. Hu and X. Wang, Chem. Commun., 2012, **48**, 2773-2775.
9. A. K. Mondal, D. Su, S. Chen, B. Sun, K. Li and G. Wang, RSC Adv., 2014, **4**, 19476-19481.
10. S. Anwar, K. S. Muthu, V. Ganesh and N. Lakshminarasimhan, J. Electrochem. Soc., 2011, **158**, A976.
11. A. Jena, N. Munichandraiah and S. A. Shivashankar, J. Power Sources, 2013, **237**, 156-166.
12. P. Elumalai, H. N. Vasan and N. Munichandraiah, J. Power Sources, 2001, **93**, 201-208.
13. W. Lei, D. Zhi Hui, W. Zheng Gong, Z. Feng Xing and J. Jian, Adv. Funct. Mater., 2013, **23**, 2758-2764.
14. P. Jeevanandam, Y. Koltypin, A. Gedanken, Y. Mastai, J. Mater. Chem., 2000, **10**, 511-514.
15. Z. Hu, L. Mo, X. Feng, J. Shi, Y. Wang and Y. Xie, Mater. Chem. Phys., 2009, **114**, 53-57.

RSC Advances Accepted Manuscript

16. C. Yuan, L. Yang, L. Hou, D. Li, L. Shen, F. Zhang and X. Zhang, J. Solid State Electrochem., 2011, **16**, 1519-1525.
17. X. Liu, R. Ma, Y. Bando and T. Sasaki, Angew. Chem. Int. Ed., 2010, **49**, 8253-8256.
18. R. Qiao, X. L. Zhang, R. Qiu, J. C. Kim and Y. S. Kang, Chem. Eur. J., 2009, **15**, 1886-1892.
19. M. Rajamathi, P. V. Kamath and R. Seshadri, Mater. Res. Bull., 2000, **35**, 271-278.
20. V. Gupta, S. Gupta and N. Miura, J. Power Sources, 2008, **177**, 685-689.
21. L.-B. Kong, J.-W. Lang, M. Liu, Y.-C. Luo and L. Kang, J. Power Sources, 2009, **194**, 1194-1201.
22. S. B. Kulkarni, A. D. Jagadale, V. S. Kumbhar, R. N. Bulakhe, S. S. Joshi and C. D. Lokhande, Int. J. Hydrogen Energy, 2013, **38**, 4046-4053.
23. M. S. Yarger, E. M. Steinmiller and K. S. Choi, Chem. Commun., 2007, **2**, 159-161.
24. G. H. A. Therese and P. V. Kamath, Chem. Mater., 2000, **12**, 1195-1204.
25. W. Simka, J. Piotrowski, G. Nawrat, Electrochim. Acta, 2007, **52**, 5696–5703.
26. F. Cao, G. X. Pan, P. S. Tang and H. F. Chen, J. Power Sources, 2012, **216**, 395-399.

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Figures Captions

Fig. 1 X-ray diffraction patterns of as-deposited $Co(OH)_2$ on SS substrate with different urea content in the nitrate bath. ∗ indicate peaks of SS substrate.

Fig. 2 FT-IR spectra of as-deposited $Co(OH)_2$ with different urea contents scraped from the SS electrode.

Fig. 3 Schematics of change of basal length of $Co(OH)_2$ upon addition of urea, (a) without addition of urea and (b) with the addition of urea.

Fig. 4 FE-SEM images on the surface of pure $Co(OH)_2$ (a), 2 wt.% (b), 4 wt.% (c), and 8 wt.% (d) urea-doped $Co(OH)_2$ samples.

Fig. 5 Cyclic voltammograms of the pure and each of the urea-doped $Co(OH)_2$ electrodes at scan rate of 5 mV s^{-1} recorded in 1M KOH.

Fig. 6 (a) Charge-discharge curves of pure and each of the urea-doped $Co(OH)_2$ electrodes at a current of 0.5 mA in 1M KOH and (b) Dependence of specific capacitance on the urea content.

Fig. 7 Cyclic voltammograms of the 2 wt.% urea-doped $Co(OH)_2$ electrode at scan rates 5, 20, 50, 80 and 100 mV s^{-1} recorded in 1M KOH.

Fig. 8 (a) Charge-discharge curves of the 2 wt.% urea-doped $Co(OH)_2$ at currents of 0.5, 1, 2, 3, and 5 mA in 1M KOH and (b) Dependence of specific capacitance on discharge current.

Fig. 9 Ragone plot for the pure $Co(OH)_2$ and the 2 wt.% urea-doped $Co(OH)_2$ electrodes.

Fig. 10 Cycle life data of the pure $Co(OH)_2$ and the 2 wt.% urea-doped $Co(OH)_2$ electrodes obtained at current of 5 mA.

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Figure 1

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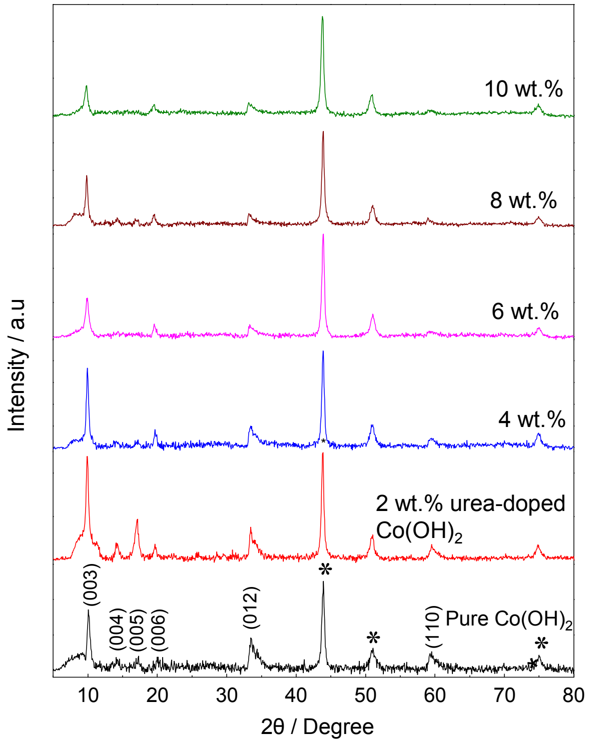

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Figure 2

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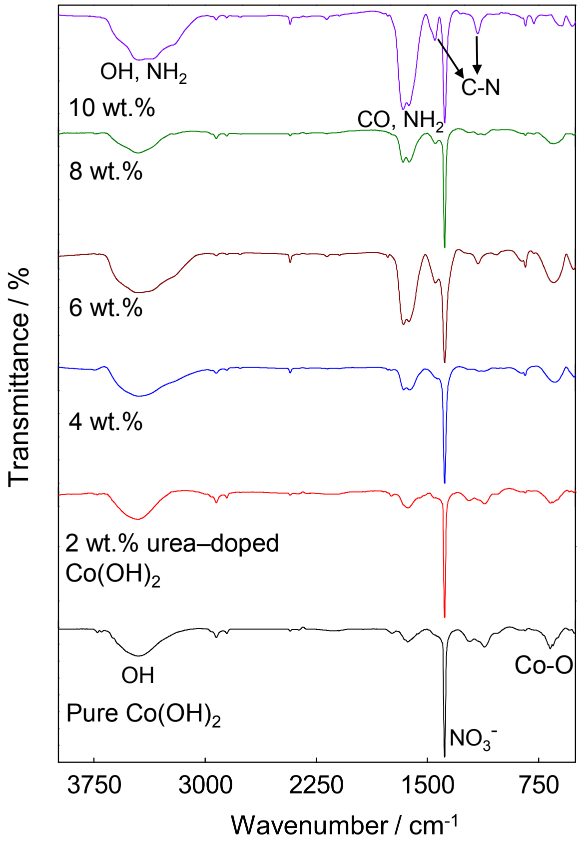

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Figure 3

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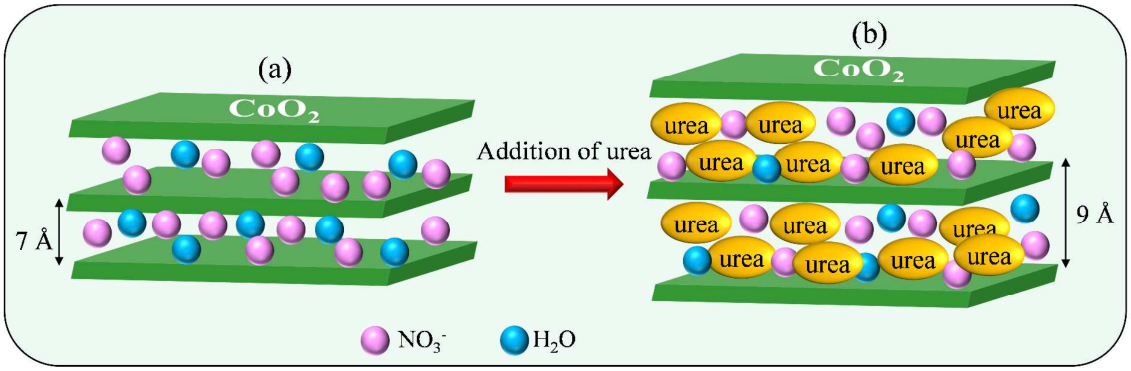

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Figure 4

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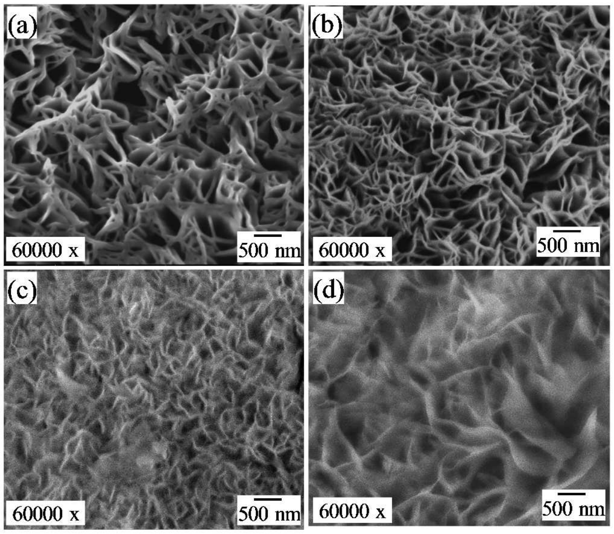

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Figure 5

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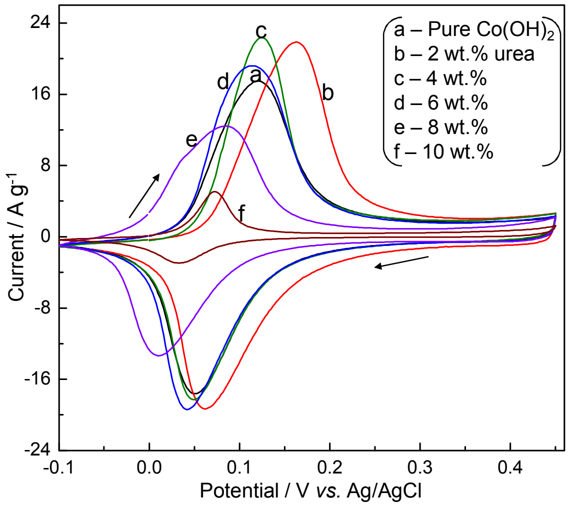

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Figure 6

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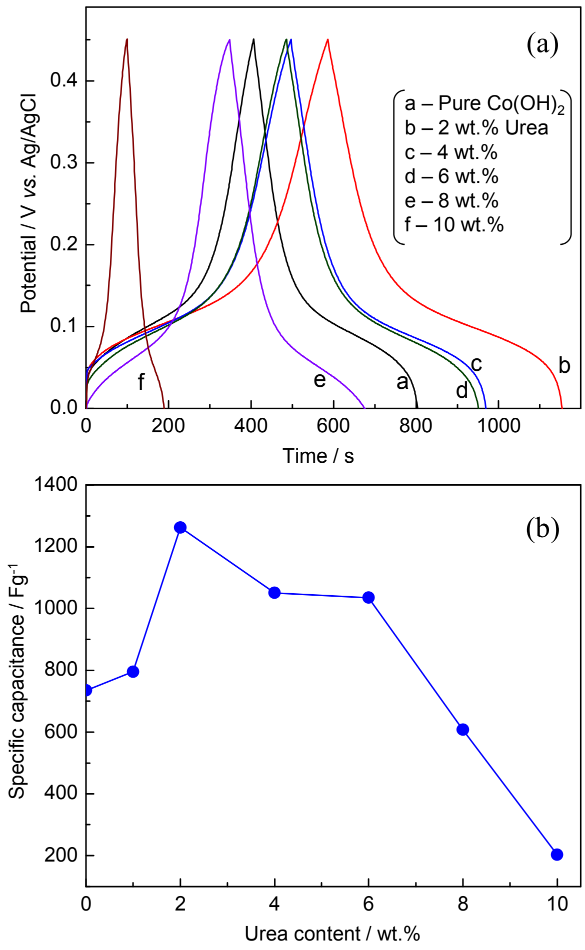

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Figure 7

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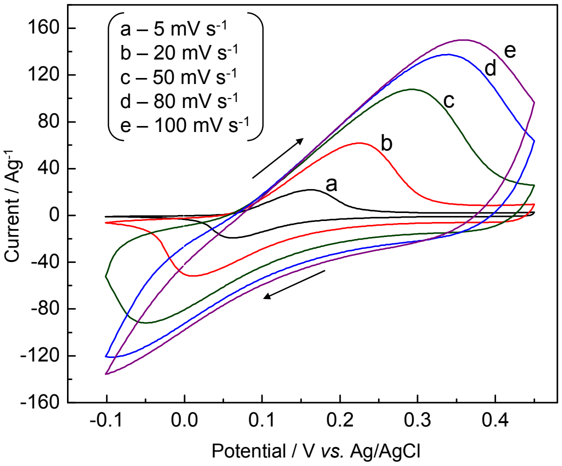

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Figure 8

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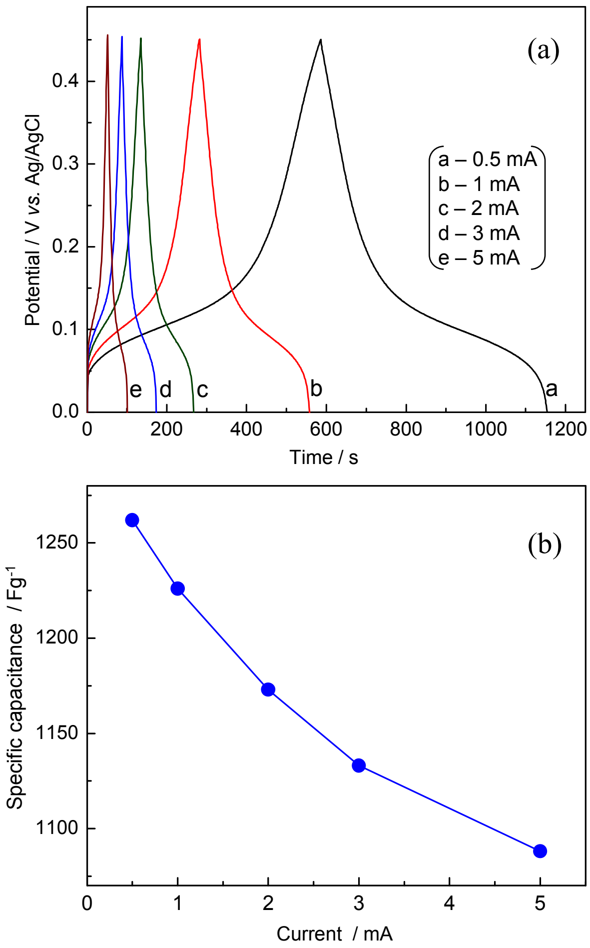

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Figure 9

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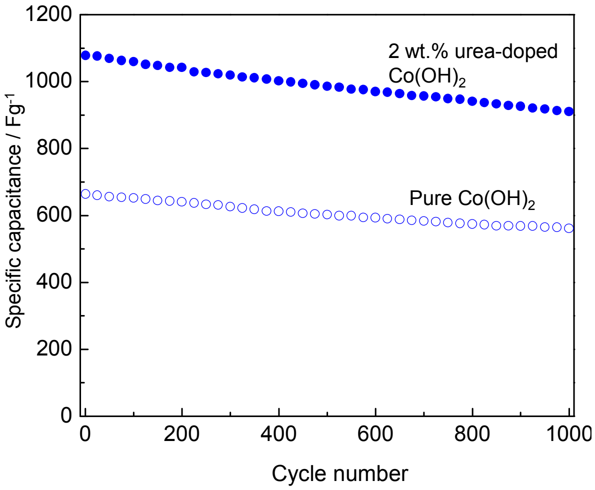

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Figure 10

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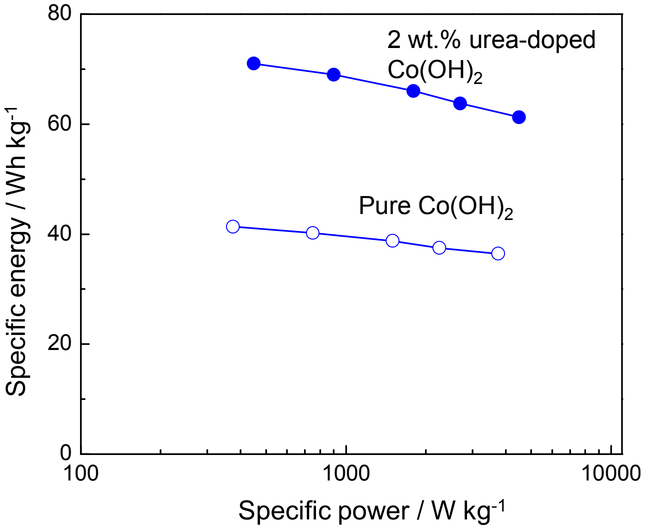

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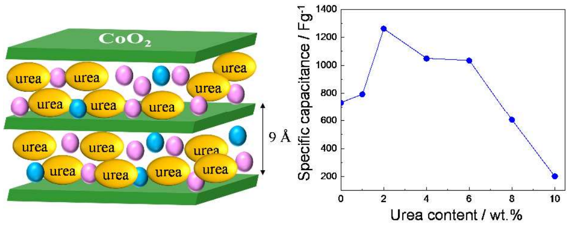
Tunable Supercapacitor Performances of Potentiodynamically Deposited Urea-doped Cobalt Hydroxide

P. Vinothbabu and P. Elumalai



The influence of basal length of $Co(OH)_2$ on supercapacitor performances was examined in detail by adding simple urea molecule during deposition. It was observed that the specific capacitance of $Co(OH)_2$ could be tuned from 700 to 1200 Fg^{-1}. The high specific capacitance was attributed to better access of electrolyte.

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