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$CoCl_2$ Designed as Excellent Pseudocapacitor Electrode Materials

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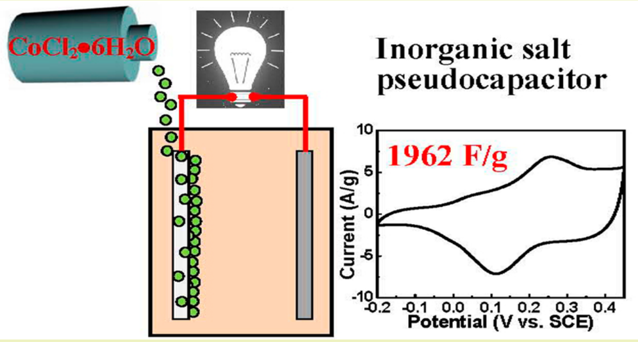
ABSTRACT: The major limitation of supercapacitors is their low energy densities compared with battery systems. However, there has not been an advanced charge storage mechanism for increasing the electrochemical performance of pseudocapacitors. For the first time, we reported that water-soluble $CoCl_2$ electrodes can show a reversible redox reaction of $Co^{2+} \leftrightarrow Co^{3+} \leftrightarrow Co^{4+}$ on the electrode and deliver very high specific pseudocapacitance of ~1962 F/g. Commercial $CoCl_2$ salt was used directly as pseudocapacitor electrodes in an aqueous electrolyte neglecting the complex synthesis procedures. We further provided electronegativity as a theoretical guideline to identify the promising active metal cations in our pseudocapacitor system. The new charge storage mechanism based on active cations offers critical insights to the rational design of a new generation of energy storage devices.



KEYWORDS: *Supercapacitor, Inorganic salt, Pseudocapacitor, $CoCl_2$, Ultrahigh specific capacitance, Active metal cation*

■ INTRODUCTION

Supercapacitors are highly desirable energy storage devices because they can deliver high levels of electrical power and offer long operating lifetimes.[1−3] The electrochemical double-layer capacitor is the first kind of supercapacitor that can store charge electrostatically using reversible adsorption of ions of electrolyte onto active materials, e.g., carbon materials.[4−7] The pseudocapacitor uses the fast reversible redox reaction at the surface of active materials, in which the valence electrons of electroactive materials are transferred across the electrode/electrolyte interface, resulting in a potential-dependent capacitance.[4] The major limitation of supercapacitors is their low energy densities compared with battery systems. One attempt was made to discover new electrode materials and advanced nanostructured materials to increase the specific capacitance in the past couple of years.[1,2] For example, nanostructured materials, metal/oxide hybrid materials, graphene/oxide hybrid materials, thin-film electrodes, and complex heterostructured nanomaterials have been designed to satisfy these demands.[8−10] However, there has not been an advanced charge storage mechanism for the improvement of electrochemical performance of pseudocapacitors.

The pseudocapacitive behavior is associated primarily with the redox reactions of the cations or changes in oxidation states of the cations in electrode materials during operation.[4] The most investigated candidates are metal oxides/hydroxides where metal ions have multiple valence states, which includes materials such as NiO, $Ni(OH)_2$, MnO_2, Co_3O_4, $Co(OH)_2$, and RuO_2.[8,11−16] It is valuable to study the pseudocapacitance of soluble cations in inorganic pseudocapacitor electrodes for further understanding the complex charge storage mechanism. However, the commercial water-soluble inorganic salts with multiple valence state metal ions have not been explored in regard to their pseudocapacitance in aqueous electrolytes. Recently, we have demonstrated that $CuCl_2$ electrodes can show electrochemical activity in a KOH electrolyte and deliver ultrahigh specific capacitance.[17]

Herein, we demonstrated that water-soluble $CoCl_2$ salt electrodes can show a fast and reversible redox reaction of $Co^{2+} \leftrightarrow Co^{3+} \leftrightarrow Co^{4+}$ and deliver very high specific pseudocapacitance of ~1962 F/g. The commercial $CoCl_2$ salt was used directly as pseudocapacitor electrodes in aqueous electrolytes, and the process is easily scalable and highly economical. The results challenge the view that the synthesis of advanced materials is an important step to increase the specific capacitance of inorganic pseudocapacitors.

■ EXPERIMENTAL SECTION

Construction of Supercapacitors and Electrochemical Measurement. Working electrodes were prepared by mixing $CoCl_2{\cdot}6H_2O$ salts, acetylene black, and poly(vinylidene fluoride) (PVDF) in a weight ratio of 80:10:10 with N-methyl-2-pyrrolidone as the solvent. Briefly, the resulting slurry was pasted onto a sheet of

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nickel foam and dried at 70 °C for 24 h. Finally, the nickel foam was pressed at 10 MPa. All electrochemical experiments were carried out using a classical three-electrode configuration in a 2 M KOH electrolyte under normal atmosphere. The saturated calomel electrode (SCE) was used as the reference electrode and Pt wire as a counter electrode. The cyclic voltammetry (CV) and galvanostatic charge–discharge measurements were carried out by an electrochemical workstation (CHI 660D).

Electrode Characterization. The electrodes were characterized by field-emission scanning electron microscopy (FESEM, Hitachi-S4800).

■ RESULTS AND DISCUSSION

$CoCl_2$ electrodes were prepared by pasting a mixture of commercial $CoCl_2·6H_2O$, acetylene black, and poly(vinylidene fluoride) (PVDF) on Ni foam and measured in a 2 M KOH electrolyte with a three-electrode configuration. The electrochemical performance was investigated by cyclic voltammetry (CV) and galvanostatic charge–discharge as shown in Figure 1. As we know, the inorganic salt is easily dissolved in aqueous solution, which cannot show electrochemical activity. However, in our present reaction system, the $CoCl_2$ electrodes indeed showed a pseudocapacitive characteristic and anomalous specific capacitance (Figure.1).

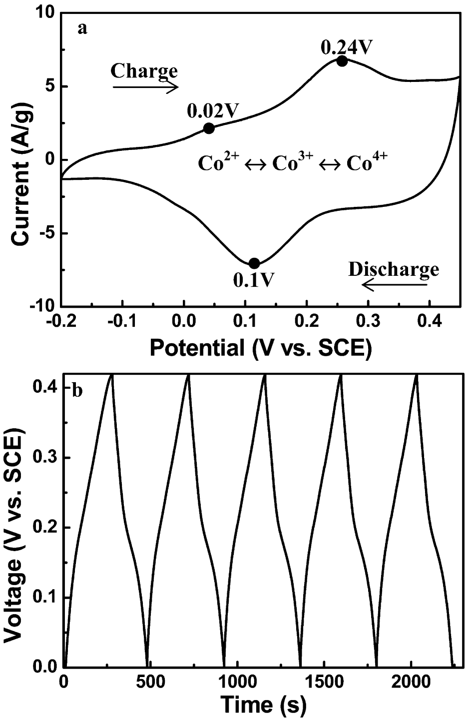


Figure 1. Electrochemical performance. (a) Cyclic voltammograms (current density versus potential) and (b) charge–discharge curves of the inorganic $CoCl_2$ salts electrodes. Redox peaks were present in the CV curve, which confirm the pseudocapacitance reaction mechanism. The CV curve was obtained at scan rate of 10 mV/s and potential range of 0–0.45 V, while the charge–discharge curves were measured at current density of 1 A/g and potential range of 0–0.42 V. All data are taken in a 2 M KOH solution at room temperature.

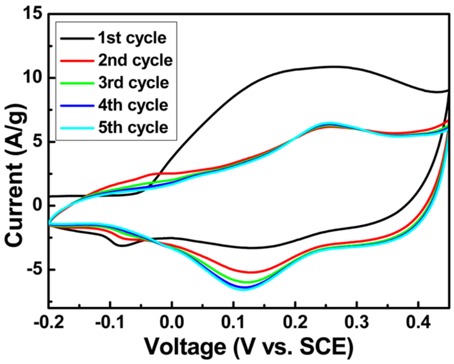


Figure 2. Cyclic voltammograms (current density versus potential) showing the evolution processes of $CoCl_2$ electrodes at a scan rate of 10 mV/s and potential range of 0–0.45 V. The redox peaks appeared after the first charge–discharge cycle. All data are taken in a 2 M KOH solution at room temperature.

CV curves were used to probe the charge storage mechanism of $CoCl_2$ electrodes. A pair of cathodic and anodic peaks is clearly observed with the scan rate of 10 mV/s (Figure 1a). The multiple peaks at different potentials correspond to the formation of a number of cobalt oxide phases with different oxidation states. The following reversible reactions can occur during the redox process in the CV study.[15,18]

$$Co_3O_4 + OH^- + H_2O \leftrightarrow 3CoOOH + e^- \quad (1)$$

$$CoOOH + OH^- \leftrightarrow CoO_2 + H_2O + e^- \quad (2)$$

The anodic peaks (positive current) and cathodic peaks (negative current) in the CV curves originate from the oxidation and reduction processes of the cobalt cation, which indicate that the capacitance characteristics are mainly governed by Faradaic redox reactions. The anodic peaks occurred around 0.02 V and 0.24 V, indicating an oxidation process related to the oxidation of Co(II) → Co(III) and Co(III) → (IV), whereas the cathodic peaks correspond to a reduction process following the Faradaic reduction reactions from Co(IV) through Co(III) to Co(II). The nonrectangular shapes of the CV curves reveal that the charge storage is a characteristic of the pseudocapacitance process originating from the reversible redox reactions of cation.

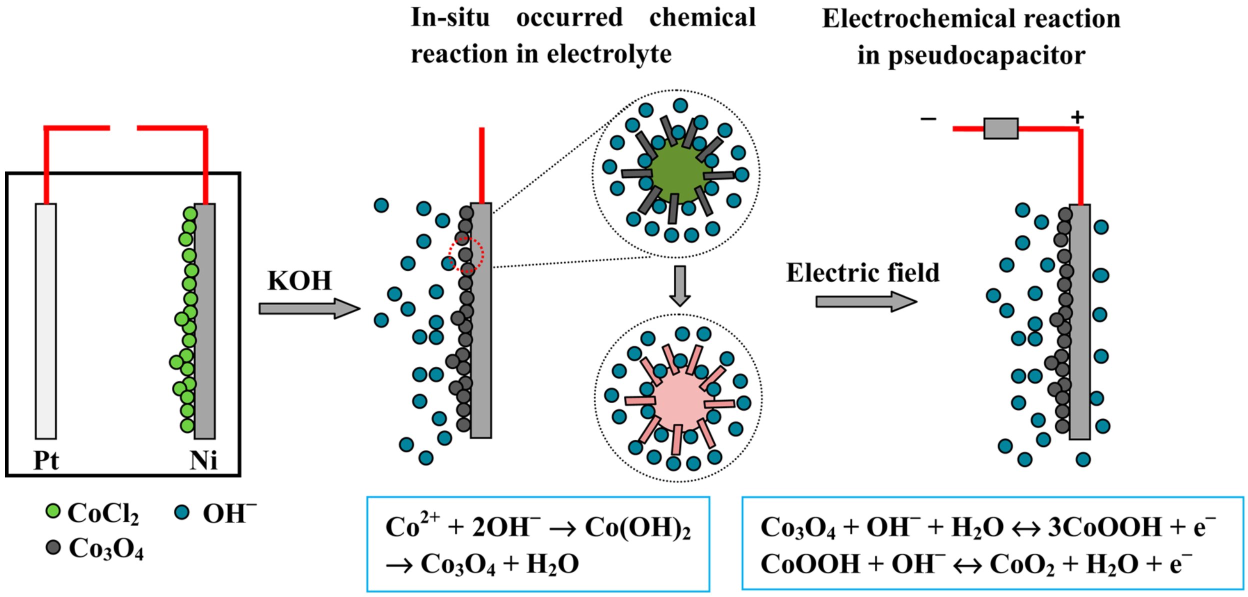
Figure 1b shows the galvanostatic charge–discharge curves. The value of the specific capacitance was obtained from the charge–discharge measurements according to the following equation[19]

$$SC = \frac{I\Delta t}{m\Delta E} \quad (3)$$

where I is the current used for charge–discharge in A, Δt is the time elapsed for the discharge cycle in s, m is the mass of the active electrode material in g, and ΔE is the voltage interval of the charge or discharge in V. According to the charge–discharge curves under galvanostatic conditions, the high specific capacitances of 1962 F/g at the current density of 1 A/g and the potential window of 0.42 V can be obtained based on the weight of active cations of Co^{2+}. The present results prove that the commercial inorganic salt indeed show electrochemical activity in alkaline electrolyte, which can challenge the view that the synthetic solid materials can only show the specific capacitance during inorganic pseudocapacitors.

To find the reaction mechanism of $CoCl_2$ electrode, the electrochemical reaction processes of $CoCl_2$ electrodes were detected by the initial CV response from the first to fifth cycles (Figure 2). After the second cycle, the redox peaks gradually appear. It is confirmed that the pseudocapacitance of the Co^{2+}

Scheme 1. Inorganic Salt Pseudocapacitor[a]



[a] Schematic illustration of the transformation of $CoCl_2$ supercapacitors in 2 M KOH when chemical reactions and electrochemical reactions occurred. When dipped into the KOH electrolyte, the $CoCl_2$ electrode underwent an in situ chemical reaction to convert into the electrochemical active $Co(OH)_2$ and Co_3O_4. Thus, electrochemical energy storage can occur through the Faradic redox reaction in the pseudocapacitance mechanism.

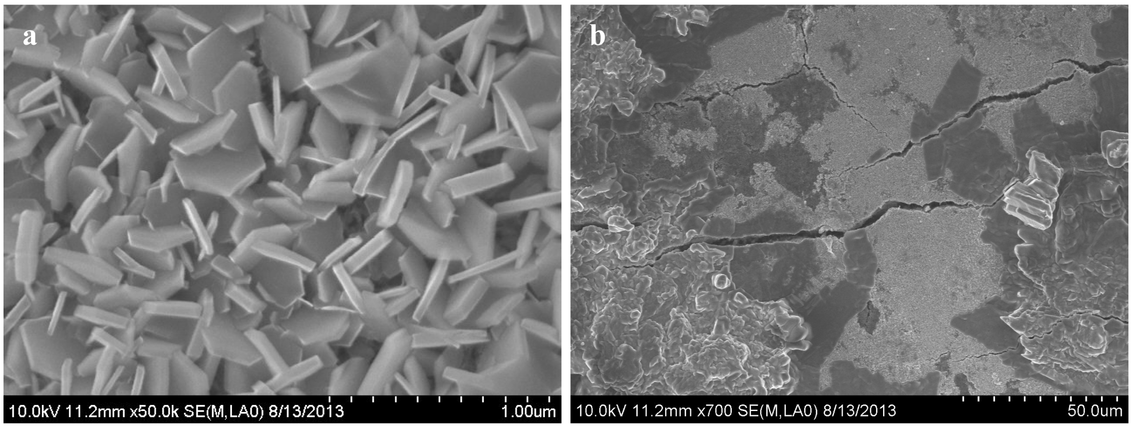


Figure 3. Microstructure characterization. (a) Enlarged and (b) large-scale SEM images of the $CoCl_2$ electrode after electrochemical measurement. Plate-like products were present at the surface of electrode.

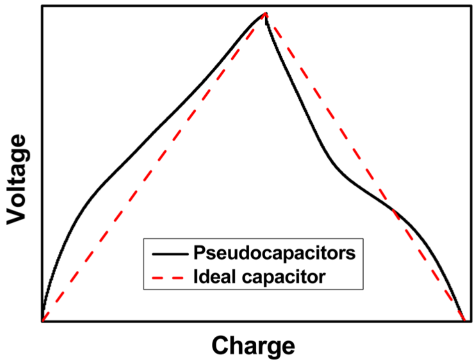


Figure 4. Scheme potential profiles of supercapacitor devices: pseudocapacitors and ideal electrical double-layer capacitors. The ideal electrical double-layer capacitor is usually characterized by a linear charge−discharge curve (dotted line). The practical pseudocapacitor often shows a nonlinear charge−discharge curve (solid line).

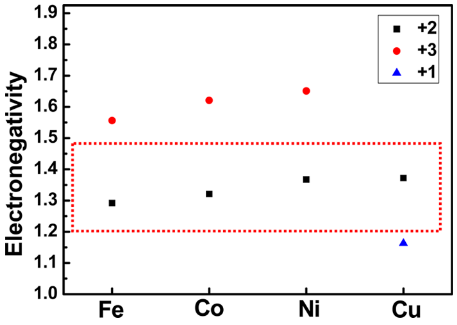


Figure 5. Electronegativity identification of active cations in our water-soluble inorganic salt pseudocapacitors. Electronegativity of selected metals with different oxidation states is shown. Red line rectangle shows the promising metal cations whose salts can be used as pseudocapacitors.

Table 1. Pseudocapacitance of Selected Metal Oxides and Hydroxides in the Literature

material	electrolyte	charge storage reaction	theoretical capacitance (F/g)
Co_3O_4	KOH, NaOH	$Co_3O_4 + OH^- + H_2O \leftrightarrow 3CoOOH + e^-$ $CoOOH + OH^- \leftrightarrow CoO_2 + H_2O + e^-$	3560 (0.45 V)
$Co(OH)_2$	KOH, NaOH	$Co(OH)_2 + OH^- \leftrightarrow 3CoOOH + H_2O + e^-$ $CoOOH + OH^- \leftrightarrow CoO_2 + H_2O + e^-$	3460 (0.6 V)
RuO_2 H_2O	H_2SO_4, Na_2SO_4	$RuO_2 + xH^+ + xe^- \leftrightarrow RuO_{2-x}$ (OH_x) $(0<x<2)$	1200−2200 (1.23 V)

Table 2. Specific Capacitance of Co^{2+} Cation Pseudocapacitor

active ion	Faradic reaction	theoretical specific capacitance (F/g)	practical specific capacitance (F/g)
Co^{2+}	$Co^{2+} \leftrightarrow Co^{3+}$ (1e) $\leftrightarrow Co^{4+}$ (2e)	3898 (1e, 0.42 V) 7797 (2e, 0.42 V)	1962

electrode is indeed promoted by the electrochemical reaction. $CoCl_2$ electrodes in the KOH electrolyte can show fast and reversible redox reactions, which further prove that inorganic salts can serve as promising pseudocapacitance electrodes.

When the electrodes were dipped in the KOH electrolyte, $CoCl_2$ can react with KOH to form $Co(OH)_2$ because of the strong chemoaffinity ability of OH^- and Co^{2+} (Scheme 1).[20,21] Then, $Co(OH)_2$ was transformed to Co_3O_4 in the strong alkaline condition. Microstructures of $CoCl_2$ electrodes after electrochemical measurements were characterized by SEM (Figure 3). After the initial chemical and electrochemical reactions, the sheet-like structures were formed on the electrode (Figure 3). After the electrochemical reaction, the in situ-formed Co_3O_4 was activated, and it contributed to the high specific capacitance of the $CoCl_2$ electrode during the charge−discharge cycling. The high specific capacitance originates from the high efficiency Faradaic reaction of $Co^{2+} \leftrightarrow Co^{3+} \leftrightarrow Co^{4+}$, which is activated by the in situ chemical and electrochemical reactions on the $CoCl_2$ electrode owing to the existence of available water-soluble Co^{2+} cations in the KOH electrolyte.

In supercapacitors, electric charge is stored in the electrode material during the charge−discharge cycling.[4,22] The ideal charge−discharge curve of the double-layer capacitor is usually a linear Q-V curve (Figure.4). A new class of electrochemical capacitors, known as pseudocapacitors, has a nonlinear Q-V curve (Figure.4).[22] The fast and reversible redox reactions at the electrode surface, in combination with the formation of double-layer capacitance, allow the pseudocapacitors to store much more energy than that of conventional supercapacitors (double-layer capacitor). Figure 4 shows that our $CoCl_2$ electrodes follow the potential profiles of pseudocapacitors, where electric charge is stored at the redox reaction of $Co^{2+} \leftrightarrow Co^{3+} \leftrightarrow Co^{4+}$ during the charge−discharge cycling.

Furthermore, we can provide electronegativity as the theoretical guideline to identify the active metal cations in our pseudocapacitor system. Electronegativity has long been recognized as an attracting power between atoms (or cations) and electrons,[21,22] which now can be used to identify the active metal cations in our pseudocapacitor system. According to the ionic electronegativity scale,[23,24] the electronegativity of these active metal cations as supercapacitors is in the range of 1.25−1.4 with a +2 oxidation state (Figure 5), which can properly hold electrons during Faradaic reactions. All selected cations are in their low oxidation state and can show pseudocapacitance in a KOH solution.[17] During the pseudocapacitive reactions, metal cations were changed from the low oxidation state to high oxidation state with an increase in their electronegativities (Figure 5). The ionic electronegativity of metal cations can provide a general guideline for the selection of suitable inorganic salt electrodes for the design of future pseudocapacitors.

Traditionally, theoretical specific capacitances of inorganic pseudocapacitors are often calculated according to the transferred electric charge and weight of active electrode materials. The theoretical specific capacitance of metal oxides can be calculated as[17,25,26]

$$C = \frac{n \times F}{M \times V} \tag{4}$$

where n is the mean number of the electrons transferred in the redox reaction, F is the Faraday constant, M is the molar mass of the metal oxide, and V is the operating voltage window. The calculated theoretical specific capacitances are shown in Table 1. However, the pseudocapacitor is associated primarily with the redox reaction of cations.[4,17] Therefore, the measured and theoretical specific capacitances of inorganic salt pseudocapacitors should be calculated according to the charge and weight of the active cations. Recently, it is reported that some pseudocapacitance materials can have higher specific capacitances than their traditional theoretical specific capacitances,[14,15] which also call for a new charge mechanism and validate our present new concept. Theoretical specific capacitance of active cations can be calculated from $C_m = Q/(V \times M)$, where $Q = 9.632 \times 10^4$ C, M is molecular weight, and V is the operating voltage window. The calculated theoretical capacitances of active cations and their practical specific capacitance are shown in Table 2. Although the specific capacitance of 1962 F/g is high, it is still lower than the theoretical specific capacitance of Co cation. Much work still needs to be done to improve the electrochemical performance of pseudocapacitors. Our water-soluble $CoCl_2$ electrodes can deepen the understanding of such a new active cation charge storage mechanism, which can favor the design of the high capacitance pseudocapacitors.

■ CONCLUSIONS

In summary, for the first time, we report that water-soluble $CoCl_2$ electrodes can show a reversible redox reaction of $Co^{2+} \leftrightarrow Co^{3+} \leftrightarrow Co^{4+}$ and deliver very high specific capacitance of ~1962 F/g. The chemical and electrochemical evolution of the $CoCl_2$ electrode and its charge storage mechanism were presented. Commercial inorganic $CoCl_2$ salts can be directly used as pseudocapacitor electrodes, neglecting complex synthesis procedures, and the process is easily scalable and highly economical. Ionic electronegativity can provide a general guideline for the selection of suitable inorganic salt for the design of future pseudocapacitors. This method can be extended to a large variety of commercial inorganic salt electrodes with the guideline of ionic electronegativity.

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Notes

The authors declare no competing financial interest.

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