

# A colloidal pseudocapacitor: Direct use of $\text{Fe}(\text{NO}_3)_3$ in electrode can lead to a high performance alkaline supercapacitor system

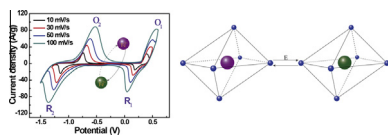


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## GRAPHICAL ABSTRACT



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## ABSTRACT

An electrochemical system including functioned  $\text{Fe}(\text{NO}_3)_3$  and alkaline electrolyte is constructed to study the charge storage mechanism upon both thermodynamic calculations and electrochemical measurements. The thermodynamic calculation results demonstrate that increasing KOH concentration of alkaline electrolyte can enhance electrolyte activity but decrease the peak potential, which agrees well with that of electrochemical measurement. The present results indicate that the proposed pseudocapacitive redox reactions are between  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  in our salt electrode of  $\text{Fe}(\text{NO}_3)_3$  system, in which the solid  $\text{Fe}^{3+}$  in  $\text{FeOOH}$  colloids serves as the active anode component and free  $\text{Fe}^{3+}$  on the colloidal electrodes serves as the cathode component. The active central ions of  $\text{Fe}^{3+}$  in  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  can be fixed on the electrodes by the surrounding ligands ( $\text{OH}^-$  and  $\text{NO}_3^-$ ) and can be in-situ transformed into colloidal  $\text{Fe}_4\text{NO}_3(\text{OH})_{11}$  and goethite ( $\alpha\text{-FeOOH}$ ). Electrochemical results indicate that the current proposed colloidal pseudocapacitor system warrants the high-efficiency utilization of electroactive central  $\text{Fe}^{3+}$  ions, showing high energy density of 58.4 Wh/kg at the power density of 8.4 kW/kg as an anode material. Meanwhile, our designed pseudocapacitor system can function well as a supercapacitor cathode. This colloidal pseudocapacitor system can offer a facile and efficient route for the design of advanced supercapacitors.

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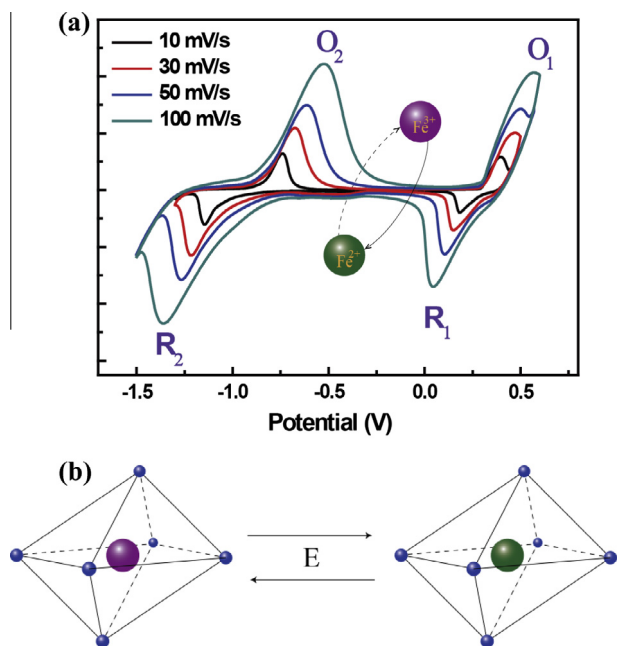
## 1. Introduction

Supercapacitors, also known as electrochemical capacitors, are considered to be state-of-the-art energy storage devices attributable to their high power density, long cycling life, and short charging time [1]. These advantages make them highly promising for use in electric vehicles, hybrid electric vehicles, and other high power electric devices [2]. As an energy storage device, supercapacitors play an important role in complementing or replacing batteries,

such as for uninterruptible power supplies and load-leveling. However, most supercapacitors can only deliver an unsatisfactory energy density (about 5 Wh/kg) [3]. Therefore, current research work on supercapacitors has been mainly focused on the enhancement of energy density to make it comparable to that of batteries [4,5]. Transition metal oxide, nitride and conducting polymer electrode materials for supercapacitors are based on pseudocapacitive charge storage mechanism, whose energy density usually exceeds that of carbon based electric double layered capacitors [6,7]. Thus a strong motivation for studying and developing pseudocapacitor is that it can lead to both high energy and high power density in the same electrode material [8].

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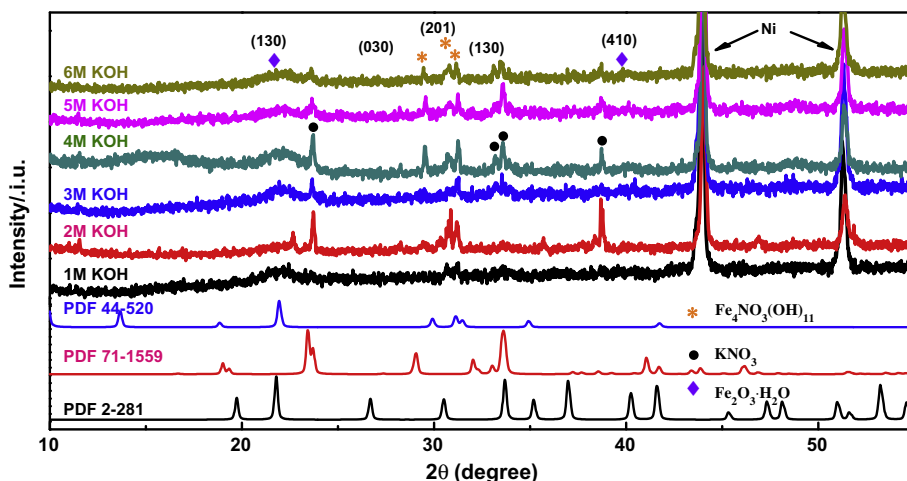
**Scheme 1.** (a) Illustration showing the reversible electrochemical redox reactions between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in  $\text{Fe}(\text{NO}_3)_3$ -based electrode and KOH electrolyte with a wide voltage window of  $-1.5$  to  $0.6$  V. (b) The iron cations can exist in the form of complexes, and the central cations can take part in Faradaic reaction.

At present, three kinds of charge storage mechanisms for pseudocapacitor electrodes have been identified [1]. The first one is underpotential deposition, which involves the adsorption of ions from the electrolyte as a monolayer on the electrode material surface. The underpotential deposition of lead on the surface of a gold electrode is a classic example [9]. The second mechanism of pseudocapacitance involves redox reactions at the surface of the electrodes, e.g., proton exchange in the surface of  $\text{RuO}_2$ . Redox pseudocapacitance can produce when ions are electrochemically adsorbed onto the surface or near the surface of an electroactive material with a concomitant Faradaic charge-transfer [8]. And the third one relies on the fast reversible intercalation of ions into the tunnels or layers of a redox-active material, such as  $\text{Nb}_2\text{O}_5$  and  $\gamma\text{-FeOOH}$ , accompanied by a Faradaic charge-transfer without crystallographic phase change [10,11]. Overall, all the pseudocapacitive behavior is associated primarily with the redox reactions, or changes in oxidation states of the cations [12].

Iron based electrode materials have been receiving considerable attention due to their low cost, abundance in nature and being environmentally benign [13]. Besides, iron oxides possess high hydrogen evolution potential in aqueous electrolyte and thus make them have wide voltage window in the negative potential region [14].  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{FeOOH}$  materials have been widely investigated among various pseudocapacitor electrode materials [15–18]. As reported in literature,  $\gamma\text{-FeOOH}$  nanosheets showed outstanding pseudocapacitive performance with the extraordinary power density of  $9$  kW/kg, specific capacitance of  $219.5$  F/g at the current density of  $12.6$  A/g, and good rate performance. The assembled asymmetric supercapacitor of  $\text{MnO}_2/\gamma\text{-FeOOH}$  delivered a high power density of  $16$  kW/kg at the energy density of  $37.4$  Wh/kg [11]. Specific capacitances for core-shell  $\alpha\text{-FeOOH}$  and  $\alpha\text{-Fe}_2\text{O}_3$  materials were found to be  $160$  F/g and  $200$  F/g, respectively. Moreover, these iron oxide composite electrodes exhibited excellent cycling performance with more than 99% capacitance retention over 500 cycles [19].  $\text{Fe}_3\text{O}_4$  nanoparticles/carbon black nanocomposite electrode showed high specific capacitance of  $300$  F/g and exhibited excellent long cycling life with 98.5% specific capacitance retention after 10,000 cycles [20]. Porous  $\alpha\text{-Fe}_2\text{O}_3$  electrode showed high capacitance of  $193$  F/g in  $0.5$  M  $\text{Na}_2\text{SO}_3$  at the current density of  $1$  A/g. The capacitance retention after 1000 cycles was about 92% of the initial capacitance at a current density of  $2$  A/g [21]. Nanostructured electrode materials are of importance for enhancing the capacitive behavior of supercapacitors because they can have large surface areas for charge storage and lead to fast redox reactions [22,23].

The design of ionic-state colloidal electrode, which consists of electroactive cationic media within the whole colloids, can represent a promising strategy to increase the energy density of pseudocapacitors without the compromise of power and lifetime performance [24]. Our previous works have confirmed that reactive cations of  $\text{Fe}^{3+}$  can be transformed into colloids through in-situ coprecipitation and electrochemical redox reaction [25,26]. In addition, various inorganic metal salts have been designed as pseudocapacitive colloids and ultrahigh specific capacitances can be achieved [12,27–32].

In the present work, the  $\text{Fe}(\text{NO}_3)_3$  salt based colloids exhibited high electrochemical performance and can be used as both cathode and anode materials for pseudocapacitors in KOH electrolytes. In addition, the variation of reduction/oxidation potential agrees with the thermodynamic calculation results based on Nernst equation in  $1\text{--}6$  M KOH electrolytes. The charge storage in our functionality of  $\text{Fe}(\text{NO}_3)_3$  electrode system is based on Faradaic reaction between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . As an cathode, the



**Fig. 1.** XRD patterns of  $\text{Fe}(\text{NO}_3)_3$ -based electrodes after electrochemical tests in 1, 2, 3, 4, 5, and 6 M KOH electrolytes.

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