Materials Research Bulletin 96 (2017) 485–490

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Intercalation and electrochemical behaviors of layered FeOCl cathode material in chloride ion battery

Tingting Yu[a], Xiangyu Zhao[a,b,*], Liqun Ma[a], Xiaodong Shen[a,b,c]

[a] College of Materials Science and Engineering, Nanjing Tech University, 5 Xinmofan Road, 210009 Nanjing, China
[b] Jiangsu Collaborative Innovation Center for Advanced Inorganic Functional Composites, Nanjing Tech University, 5 Xinmofan Road, 210009 Nanjing, China
[c] State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, 5 Xinmofan Road, 210009 Nanjing, China

ARTICLE INFO

Article history:
Received 28 February 2017
Received in revised form 13 March 2017
Accepted 29 March 2017
Available online 22 May 2017

Keywords:
A. Layered compounds
B. Intercalation reactions
A. Iron oxychloride
Chloride ion batteries
D. Electrochemical properties

ABSTRACT

Layered metal oxychloride FeOCl is considered as one of the promising cathode materials for chloride ion batteries due to its abundant elemental components and high capacity. Herein, we report the intercalation and electrochemical behaviors of the layered FeOCl material in the chloride ion battery. The intercalation of *N*-methyl-2-pyrrolidinone into the FeOCl layers has been found during the drying of the electrode coating at 373 K. The electrolyte component can also be intercalated into the FeOCl layers at 298 K without charge and discharge. The intercalation by these organic components results in evident expansion of the layers. Repeated charge and discharge cycling contributes to an activation of the FeOCl electrode and thus an increase of the discharge capacity. The results of elemental analysis and Fourier transform infrared spectroscopy confirm the chloride ion transfer of the FeOCl electrode during cycling.

1. Introduction

Many advanced electrode materials have been developed for rechargeable batteries [1–6]. The layer-structured materials such as graphite and transition-metal-based compounds have drawn great attention in the intercalation reactions and also the preparation of two-dimensional materials [7–11]. FeOCl is a member of the layer-structured compounds and its adjacent layers are stacked by a van der Waals interaction. Many materials such as alkali metals [12], organic molecules [13,14], organometallics [15] and fullerene-derivative [16] could be intercalated into the layers of FeOCl. The intercalation reaction favored the enhancement in the electrical conductivity of FeOCl, which is a Mott insulator material and has a high electrical resistivity of $10^7\,\Omega$ cm [17,18]. For instance, a much lower electrical resistivity of $10\,\Omega$ cm could be obtained by the intercalation of $FeCp_2$ into the FeOCl [15]. The layers of FeOCl orient perpendicular to the *b* direction, which formed by the sharing of O—O and O—Cl edges of *cis*-$FeCl_2O_4$ octahedra [19], and the outermost atoms on each side of the layers are chlorine atoms. Moreover, removal of the chlorine atoms in FeOCl would bring about a large Gibbs free energy change and thus FeOCl has been proposed as the cathode material of chloride ion batteries [20].

Some electrochemical couples, including metal chloride/metal [21], metal oxychloride/metal [20,22–24] and chlorine-doped polymer/metal [25], have been reported for chloride ion batteries. Metal oxychloride and chlorine-doped polymer cathodes both have higher stability and lower volumetric change than the metal chloride cathode. FeOCl as a metal oxychloride cathode has a high theoretical capacity of about 250 mAh g^{-1} and abundant elemental components. Its electrochemical reactions based on chloride ion transfer have been proved by the TEM/EDS, XPS and electrochemical methods together with DFT calculations [20,23]. Recently, Ping et al. found that the electrolyte component could be intercalated into the layers of vanadium oxychloride (VOCl) during the first discharge [24]. This led to irreversible expansion of the VOCl layers during cycling. FeOCl has a similar layered structure with VOCl. However, this kind of intercalation process and the following structural change during cycling was not concerned in the FeOCl/carbon composite materials [23].

In this work, a systematic research on the structural change of the layered FeOCl material during the electrode preparation process and in a chloride ion battery (CIB) system has been performed. Both the *N*-methyl-2-pyrrolidinone and the electrolyte component have been found to be intercalated into the FeOCl

---

[*] Corresponding author at: College of Materials Science and Engineering, Nanjing Tech University, 5 Xinmofan Road, 210009 Nanjing, China.
E-mail address: xiangyu.zhao@njtech.edu.cn (X. Zhao).

http://dx.doi.org/10.1016/j.materresbull.2017.03.070
0025-5408/

layers, leading to evident structural and morphology changes. The electrochemical behaviors and the corresponding post analysis of the FeOCl electrodes were also investigated.

2. Experimental

The preparation of FeOCl using a chemical vapor transport method at 643 K has been reported in the previous work [20]. The anhydrous ionic liquids of 1-Butyl-1-methylpiperidinium bis (trifluoromethylsulfonyl)imide ($PP_{14}TFSI$, 99%, IoLiTech) and 1-Butyl-1-methylpiperidinium chloride ($PP_{14}Cl$, 99%, IoLiTech) were all dried at 358 K for 72 h under vacuum.

X-ray Powder diffraction (XRD) was performed using a Rigaku SmartLab diffractometer with Cu-Kα radiation. The morphology and composition of the samples were characterized by a field-emission scanning electron microscopy (Ultra55, FE-SEM) incorporated with an energy-dispersive X-ray spectroscopy (EDS). Fourier transform infrared spectroscopy (FTIR) spectra were obtained using a Thermo Nicolet Nexus 670 Spectrometer in the wave number range from 400 to 4000 cm^{-1}. For all the sample preparation, anhydrous acetonitrile (ACN) was used to wash the samples and remove the residue electrolyte in the glove box.

Electrochemical measurements were conducted using coin cells (CR2032) with lithium metal (Alfa Aesar) as anode. The FeOCl cathode electrodes were fabricated by mixing pure FeOCl powders, PVDF, and carbon black in the mass ratio of 60:10:30. *N*-methyl-2-pyrrolidinone (NMP) was used as the solvent for PVDF to get homogeneous slurry, which was spread on a graphite foil (17 μm, Suzhou Dasen Electronics Material Co. Ltd) and dried in a vacuum oven at 373 K for 20 h. A mixture of 0.5 M $PP_{14}Cl$ in $PP_{14}TFSI$ was used as electrolyte. Celgard 2400 film was used as separator. Discharge and charge tests were carried out galvanostatically at 10 mA g^{-1} over a voltage range between 1.6 and 3.5 V by using Arbin BT2000 multi-channel battery testing system at 298 K. The specific capacities were calculated according to the corresponding active material of FeOCl. Electrochemical impedance spectroscopy (EIS, 100 kHz–10 mHz, 10 mV) data and Cyclic voltammetry (CV, 1.6–3.5 V, 60 μV s^{-1}) were all collected by a BioLogic (VMP3) electrochemical workstation.

3. Results and discussion

Fig. 1a shows the XRD pattern and SEM image of the as-prepared FeOCl powders. All reflections of the FeOCl can be indexed and assigned to the orthorhombic layered FeOCl phase (PDF card no. 72-619) with three characteristic peaks corresponding to (010), (110) and (021) planes. The as-prepared FeOCl powders exhibit a flake-like morphology. Fig. 1b shows the discharge and charge curves of the FeOCl/Li electrode system. The discharge capacity of the FeOCl cathode increases in the initial cycles and then decreases, as shown in Fig. 1d. The FeOCl cathode shows a discharge capacity of only 44 mAh g^{-1}, which is 17.6% of the theoretical capacity at the first cycle. The maximum discharge capacity is 149 mAh g^{-1}, which is much lower than that of the FeOCl/carbon composite cathode [23]. Fig. 1c shows the CV patterns of the FeOCl/Li system. In the first cycle, there are three reduction peaks located at 2.96, 2.41 and 1.89 V, and two oxidation peaks at 2.22 and 3.18 V. In the second cycle, the reduction peak at 2.96 V shifted to a lower potential, the reduction peak at 2.41 V was weakened and the oxidation peak at 2.22 V disappeared. Upon cycling the oxidation peak at 3.18 V becomes weaker and broader. Three redox peaks suggest a multistep electrochemical reaction behavior during cycling. Similar phenomenon was reported when VOCl was used as the cathode material for CIB [24].

Ex situ XRD analysis (Fig. 2) was performed to investigate the structural evolution of the FeOCl electrodes at different electrochemical states. The diffraction peak at $2\theta = 26.5°$ is assigned to the reflection of the graphite foil current collector. The XRD patterns of the FeOCl electrodes during cycling were entirely different from that of the as-prepared FeOCl powders. The FeOCl electrode shows

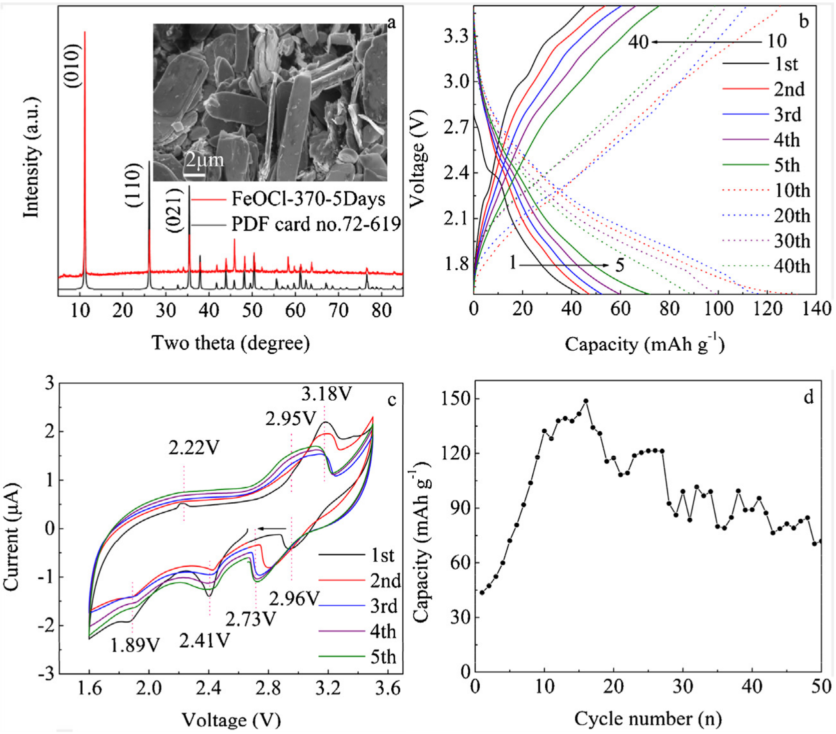

Fig. 1. a) XRD pattern and SEM image (Inset) of the FeOCl, b) Discharge and charge curves (10 mA g^{-1}), c) CV patterns (1st–5th cycles, 60 μV s^{-1}) and d) cycling performance of the FeOCl/Li electrode system using the electrolyte of 0.5 M $PP_{14}Cl$ in $PP_{14}TFSI$ at 298 K.