

# EQCM studies of composition and electrochemical performance of film prepared by electrochemical reduction of sodium ferrate

Li Zhao · Bai-Shuang Chen · Jia-Lin Zhang · Dian-Long Wang

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**Abstract** A solid film was prepared by electrodepositing on a gold-film-coated quartz crystal electrode in  $\text{Na}_2\text{FeO}_4$  solution, and characterized in 1 M  $\text{LiClO}_4$ /propylene carbonate (PC) + 1, 2-dimethoxyethane (DME; 1:1 by volume) electrolyte using electrochemical quartz crystal microbalance (EQCM). The EQCM experimental and X-ray photoelectron spectroscopy results indicate that the composition of the electrodeposited solid film prepared in the potential range of 0.18 to  $-0.57$  V vs. Ag/AgCl is  $\text{FeOOH}$ ; and almost 1 mol lithium ions can be intercalated into and then extracted from 1 mol  $\text{FeOOH}$  film during discharge/charge process in 1 M  $\text{LiClO}_4$ /PC + DME electrolyte. The discharge/charge experiment indicates that the specific capacity of  $\text{FeOOH}$  film stabilizes at a value close to its theoretical specific capacity after 20 cycles, and  $\text{FeOOH}$  film maintains a specific capacity of about  $300 \text{ mAh g}^{-1}$  at the end of 170 cycles. It is therefore concluded that the  $\text{FeOOH}$  film has a good electrochemical cycle ability in 1 M  $\text{LiClO}_4$ /PC + DME electrolyte.

**Keywords** Electrochemical quartz crystal microbalance · Ferrate · Film electrode · Lithium ion battery

## Introduction

Ferrate material was developed and used as cathode material for advanced batteries in the late twentieth century [1, 2]. Ferrate has attracted much attention from the research

community because of its energetic, yet non-toxic characteristics [3, 4]. The discharge of ferrate in nonaqueous electrolyte incorporates a three-electron reduction of Fe (VI), together with a reaction of Li ion [5]. Ferrate cathodes exhibit high initial cathodic discharge-specific capacities, for example,  $600 \text{ mAh g}^{-1}$  for  $\text{Li}_2\text{FeO}_4$ ,  $400 \text{ mAh g}^{-1}$  for  $\text{K}_2\text{FeO}_4$  and  $310 \text{ mAh g}^{-1}$  for  $\text{BaFeO}_4$  [6, 7]. However, their specific capacities fade from cycle to cycle and then stabilize at approximately 40–50% of their theoretical specific capacities [8].

And so, it was proposed to use Fe (VI/III) film prepared by electrodepositing on a conductive substrate in ferrate electrolyte to solve the problem of fast fading in specific capacity [5, 9–11]. Fe (VI/III) film exhibits a superior rechargeability in nonaqueous electrolyte, which can be cycled reversibly at a specific capacity above  $300 \text{ mAh g}^{-1}$  during the prolonged cycling [5, 8]. Although Fe (VI/III) film shows a superior electrochemical performance, its composition and reaction process in nonaqueous electrolyte have not been well understood yet so far. The three-electron reduction of Fe (VI) may produce a variety of Fe (III) oxide and oxyhydroxide species, such as  $\alpha, \gamma \text{ Fe}_2\text{O}_3$ , and  $\alpha, \beta, \gamma, \delta \text{ FeOOH}$  [12], and a variety of cation-containing ferric salts, such as  $\text{NaFeO}_2$  and  $\text{KFeO}_2$  [9]. It is therefore of great significance to have a better understanding of the composition and reaction process of Fe (VI/III) film. Electrochemical quartz crystal microbalance (EQCM) technique is a powerful tool for in situ monitoring of changes in mass in an electrochemical reaction process [13]. It has been widely used in electrochemical researches [14–17]. This technique is particularly attractive for the study on lithium ion battery [18–21], because an insertion/extraction reaction of lithium ions in active materials is always accompanied by a change in mass.

In this study, in order to have a better understanding of the composition and reaction process of Fe (VI/III) film,

L. Zhao (✉) · B.-S. Chen · J.-L. Zhang · D.-L. Wang  
School of Chemical Engineering and Technology,  
Harbin Institute of Technology,  
Harbin 150001, People's Republic of China  
e-mail: dhx907@hit.edu.cn

EQCM technique was used to determine the composition of electrodeposited Fe (VI/III) film, and to investigate the reaction process and electrochemical performance of the electrodeposited film in nonaqueous electrolyte.

## Experimental

### Reagents

The sodium hydroxide and lithium perchlorate were purchased from Tianjin Kaitong Chemical Reagents Limited Company, and the propylene carbonate (PC) and 1, 2-dimethoxyethane (DME) were purchased from Shanghai Hebao Chemical Engineering Limited Company. All the reagents were of analytical reagent grade, and were used directly without any purification. Deionized water was used throughout the experiments.

### Preparation of Fe (VI/III) film

$\text{Na}_2\text{FeO}_4$  was firstly electrosynthesized at a temperature of 20 °C in a double compartment cylindrical glass cell with iron wire of 99.9% purity used as anode and foam nickel used as cathode. Both anolyte and catholyte used was 14 M NaOH solutions. The operational current density was 10 mA cm<sup>-2</sup> and the total operational time was 4 h. An anolyte containing  $\text{Na}_2\text{FeO}_4$  was obtained at the end of electrolysis. Fe (VI/III) film was prepared in a three-electrode cell using a CHI430 electrochemical quartz crystal microbalance. A quartz crystal disk (7.995 MHz, AT cut) coated with gold film on both sides was used as the working electrode. A Pt foil was used as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode. The electrolyte was 2.7 mM  $\text{Na}_2\text{FeO}_4$  solution. A cooling water bath was used to control the temperature at 20 °C. Potentiodynamic and EQCM experiments were performed with a potential range of 0.20 to -0.86 V, and the scan rate was 2 mV s<sup>-1</sup>.

### Analysis

Surface analysis was performed by X-ray photoelectron spectroscopy (XPS), using a PHI 5700 ESCA system manufactured by Physical Electronics Industries Inc. SEM observation was performed at a voltage of 20 kV using a S4700 scanning electron microscope made in Japan.

### Electrochemical measurements

A three-electrode cell was used for EQCM measurement. A prepared Fe (VII/III) film electrode was used as the working electrode, a lithium foil was used as the counter electrode,

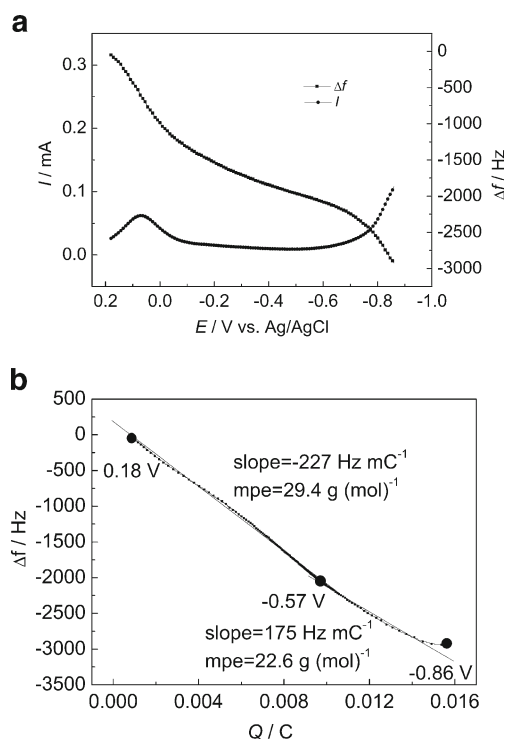
and another lithium foil was used as the reference electrode. The electrolyte used was 1 M  $\text{LiClO}_4/\text{PC} + \text{DME}$  (1:1 by volume) solution. The charge/discharge performance of Fe (VI/III) film in 1 M  $\text{LiClO}_4/\text{PC} + \text{DME}$  (1:1 by volume) electrolyte was tested using a CT-3008w battery testing system.

## Results and discussion

### EQCM measurement of the preparation of Fe(VI/III) film

Figure 1a shows the current–potential curve and EQCM frequency data for a gold film-coated quartz crystal electrode in  $\text{Na}_2\text{FeO}_4$  solution. The decrease in resonance frequency responds to the increase in mass. As the potential decreases from 0.2 V to about 0.1 V, the reduction rate gradually increases, together with the increase of mass of the gold-film-coated electrode. The reduction rate reaches its maximum at the potential of 0.09 V, and then gradually decreases. The reaction rate gets higher again when the potential lowers more than -0.6 V, which may be due to the formation of  $\text{H}_2$ , because some bubbles are observed on the surface of the gold-film-coated electrode.

The reaction in the potential range of 0.2–0.1 V is the reduction of  $\text{Na}_2\text{FeO}_4$ . EQCM was used to determine the composition of the reduction product. According to Sauerbrey



**Fig. 1** EQCM measurement of gold-film-coated quartz crystal electrode in 2.7 mM  $\text{Na}_2\text{FeO}_4$  solution at a scan rate of 2 mV s<sup>-1</sup>: **a** cycle voltammogram and EQCM frequency data and **b** plot of  $\Delta f$  versus  $Q/C$

equation, change in mass of electrode ( $\Delta m$ ) is in direct proportion to change in resonance frequency ( $\Delta f$ ).

$$\Delta m = -k\Delta f \tag{1}$$

where  $k$  is the mass sensitivity of crystal,  $1.34 \text{ ng Hz}^{-1}$  for the system under test. In an electrochemical process, the change in mass per mole of electrons can be expressed as

$$mpe = -F \frac{dm}{dQ} = -Fk \frac{df}{dQ} \tag{2}$$

where  $mpe$ ,  $F$ , and  $Q$  are change in mass per mole of electrons, Faraday constant, and electric quantity, respectively.

It can be known from Eq. 2 that  $mpe$  is in direct proportion to slope ( $df/dQ$ ) of the variation of  $\Delta f$  versus  $Q$ . The variation of  $\Delta f$  versus  $Q$  obtained from Fig. 1a is shown in Fig. 1b.

In the potential range of 0.18 to  $-0.57 \text{ V}$ ,  $mpe$  equals  $29.3 \text{ g mol}^{-1}$ , which corresponds to  $88.2 \text{ g}$  for a three-electron transfer process. If it is assumed that the reduction of  $\text{Na}_2\text{FeO}_4$  is a three-electron transfer process, and the reduction product is  $\text{FeOOH}$ , the reaction equation can be expressed as

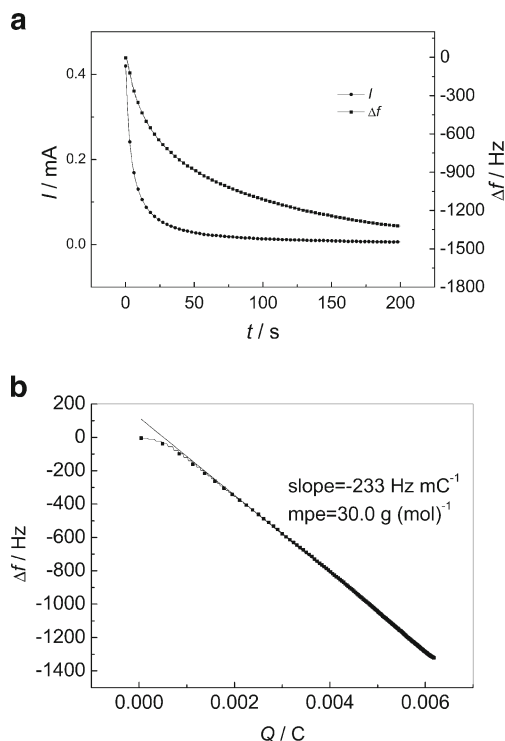


It is obvious that the transfer of 3-mol electrons will produce 1-mol  $\text{FeOOH}$ , i.e.,  $88.8 \text{ g FeOOH}$ , which is in agreement with the result of EQCM. If it is assumed that the reduction product of  $\text{Na}_2\text{FeO}_4$  is  $\text{Fe}_2\text{O}_3$  or  $\text{NaFeO}_2$ , the theoretical  $mpe$  should equal  $26.6 \text{ g mol}^{-1}$  or  $36.9 \text{ g mol}^{-1}$ , which is different to the measured one. So, reaction equation (3) denotes the actual reduction reaction of  $\text{Na}_2\text{FeO}_4$  on the gold-film-coated electrode surface. In the potential region of lower than  $-0.6 \text{ V}$ , the measured  $mpe$  is  $22.6 \text{ g mol}^{-1}$ , smaller than the theoretical one given by Eq. 3, which may be due to the formation of  $\text{H}_2$ .

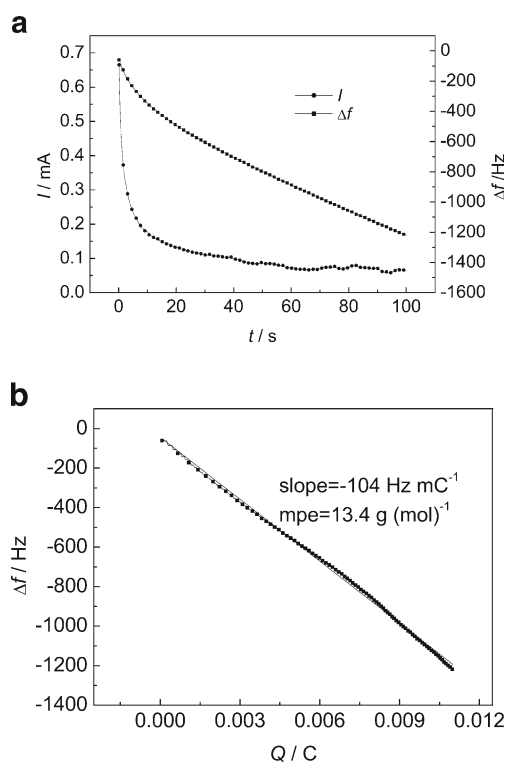
EQCM results of  $\text{Na}_2\text{FeO}_4$  reduction reaction at the potential of  $-0.50$  and  $-0.86 \text{ V}$  vs.  $\text{Ag/AgCl}$  are given in Figs. 2 and 3, respectively. It can be seen from Fig. 2 that  $mpe$  equals  $30.0 \text{ g mol}^{-1}$ , which is approximately consistent with the  $mpe$  calculated from Eq. 3. If the reduction potential is fixed at  $-0.86 \text{ V}$  (see Fig. 3),  $mpe$  is less than the theoretically calculated value based on Eq. 3. These results are in agreement with the result of Fig. 1.

### Analysis of Fe(VI/III) film

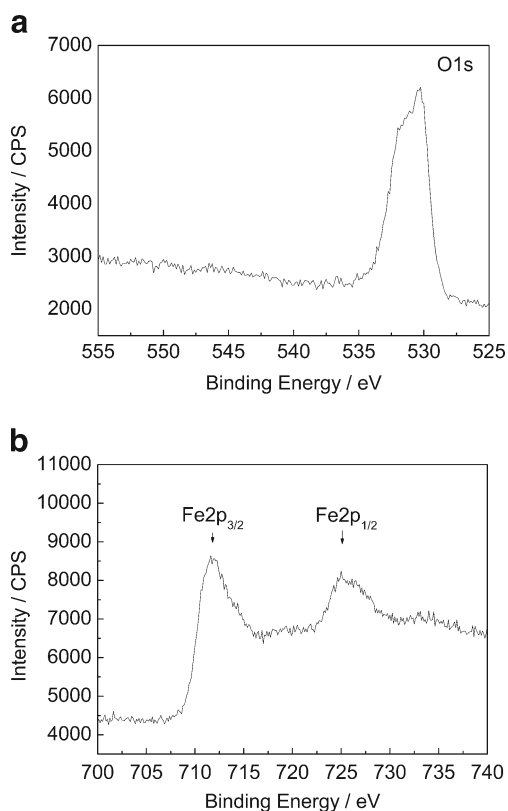
XPS was also used to analyze the composition of the electrodeposited film. Figure 4 shows the XPS spectrums of O1s and Fe2p of the electrodeposited film prepared at the potential of  $-0.50 \text{ V}$  vs.  $\text{Ag/AgCl}$ . The spectrum of O1s contains two asymmetric peaks which are the exclusive peaks of  $\text{FeOOH}$ . The positions of Fe2p peaks of the electrodeposited film are consistent with that of trivalent iron [22]. It can



**Fig. 2** EQCM measurement of gold-film-coated quartz crystal electrode in  $2.7 \text{ mM Na}_2\text{FeO}_4$  solution at a potential of  $-0.50 \text{ V}$  vs.  $\text{Ag/AgCl}$ : **a**  $I$ - $t$  curve and EQCM frequency data and **b** plot of  $\Delta f$  versus  $Q$



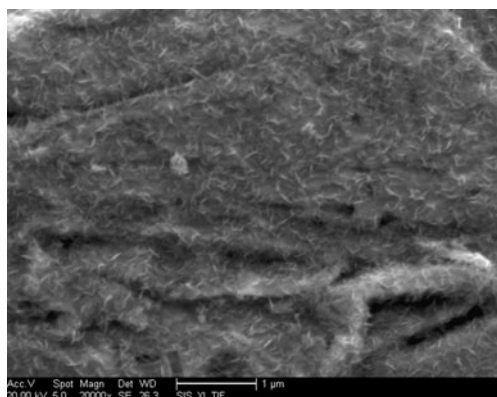
**Fig. 3** EQCM measurement of gold-film-coated quartz crystal electrode in  $2.7 \text{ mM Na}_2\text{FeO}_4$  solution at a potential of  $-0.86 \text{ V}$  vs.  $\text{Ag/AgCl}$ : **a**  $I$ - $t$  curve and EQCM frequency data and **b** plot of  $\Delta f$  versus  $Q$



**Fig. 4** XPS spectra of electrodeposited film: **a** O1s and **b** Fe2p

be concluded from EQCM and XPS results that the composition of the electrodeposited film is FeOOH instead of Fe<sub>2</sub>O<sub>3</sub> and NaFeO<sub>2</sub>, i.e., FeOOH film can be prepared in the cathodic potential region of 0.18 to  $-0.57$  V vs. Ag/AgCl on a gold-film-coated electrode.

Figure 5 presents the surface morphology of FeOOH film prepared at the potential of  $-0.50$  V vs. Ag/AgCl. It can be seen from Fig. 5 that the prepared FeOOH film has a relatively rough surface, and can be considered as a film constructed with some needle-like micro-structures of about 100–300 nm in length on the substrate.

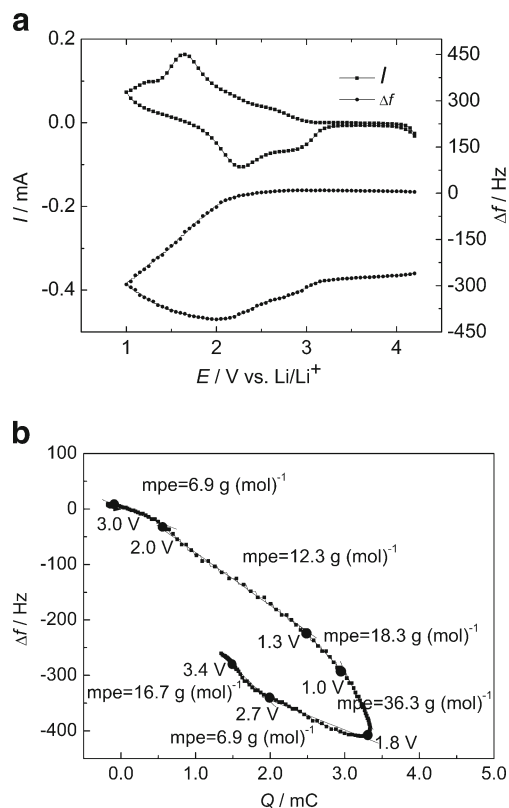


**Fig. 5** SEM image of FeOOH film prepared at potential of  $-0.5$  V vs. Ag/AgCl

### Electrochemical performance of FeOOH film

Figure 6a shows the cycle voltammogram and EQCM frequency data of FeOOH film prepared at the potential of  $-0.50$  V vs. Ag/AgCl in 1 M LiClO<sub>4</sub>/PC + DME (1:1 by volume) electrolyte at a scan rate of  $50$  mV s<sup>-1</sup>. It can be seen from Fig. 6a that the mass of the film increases with the intercalation of lithium ions in the FeOOH film during the cathodic sweep process. During the anodic sweep process, an oxidation peak is observed at 2.25 V when the potential is scanned from 1.00 to 3.50 V, which corresponds to the extraction of lithium ions from the FeOOH film. Meanwhile, the mass of the film decreases. It should be noted that a complete mass balance cannot be achieved during the complete cathodic and anodic sweep process, and the absolute value of the increase in mass during the cathodic process is always larger than the decrease in mass in the subsequent anodic process. The unbalanced mass on the FeOOH film may be attributed to the formation of SEI layer and the adsorption/desorption of solvents.

Figure 6b shows the plot of frequency change versus charge change of the prepared FeOOH film in 1 M LiClO<sub>4</sub>/PC + DME (1:1 by volume) electrolyte at a scan rate of  $50$  mV s<sup>-1</sup>. mpe is calculated and indicated for each



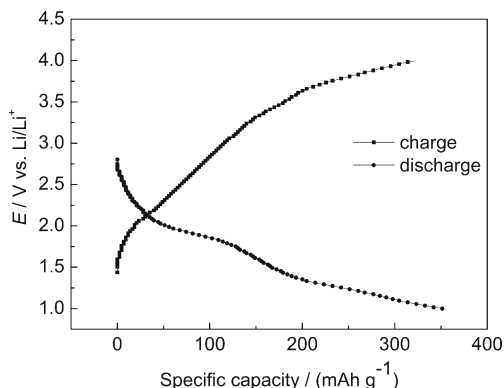
**Fig. 6** EQCM measurement of FeOOH film in 1 M LiClO<sub>4</sub>/PC + DME (1:1 by volume) electrolyte at a scan rate of  $50$  mV s<sup>-1</sup>: **a** cycle voltammogram and EQCM frequency data and **b** plot of  $\Delta f$  versus  $Q$

process. It can be seen from Fig. 6b that mpe is  $6.9 \text{ g mol}^{-1}$  when the potential is scanned from 3.0 to 2.0 V, which is in agreement with the result theoretically calculated with one electron transfer per equivalent of Li. For the cathodic potential range of 2.0–1.0 V, mpe is  $12.3 \text{ g mol}^{-1}$  (2.0–1.3 V), and  $18.3 \text{ g mol}^{-1}$  (1.3–1.0 V), respectively. The measured value of mpe is larger than the result theoretically calculated with one electron transfer per equivalent of Li, which means some other processes have taken place in these potential ranges, e.g., the formation of SEI layer and/or the adsorption of some solvent molecules on the FeOOH film electrode before their reduction [23].

The value of mpe varies with the potential region during the potential range from 1.0 to 3.4 V. mpe equals  $6.9 \text{ g mol}^{-1}$  in the potential range from 1.8 to 2.7 V, and the mass response fits well to the result theoretically calculated with one electron transfer per equivalent of Li. In other regions, side reactions increase the value of mpe. The oxidative decomposition of the solvent on the electrode surface can be the principal side reaction at a high potential. According to the mpe results, the electrochemical reaction of FeOOH in 1 M LiClO<sub>4</sub>/PC + DME (1:1 by volume) electrolyte can be expressed as



Figure 7 presents the charge/discharge curves of FeOOH film in 1 M LiClO<sub>4</sub>/PC + DME (1:1 by volume) electrolyte at 0.5 C. The cell was first discharged to intercalate lithium ions in FeOOH film, and then charged to extract ions from FeOOH film. In discharge process, the electrode potential shows an abrupt drop at the initial stage, followed by a potential plateau at around 2.0 V, and then decreases again. The discharge potential is 1.5 V at the specific capacity of  $160 \text{ mAh g}^{-1}$ , and gradually decreases to 1.0 V at the specific capacity of  $340 \text{ mAh g}^{-1}$ . The observed specific capacity is very close to the theoretical one given by Eq. 4. It can be seen from this result that, in the discharge/charge process, almost one lithium ion can be intercalated into and



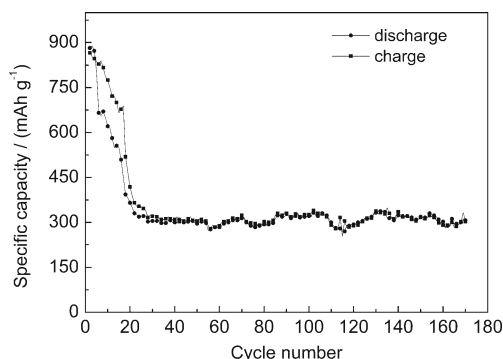
**Fig. 7** Charge and discharge curves of FeOOH film in 1 M LiClO<sub>4</sub>/PC + DME (1:1 by volume) electrolyte at a current rate of 0.5 C

then extracted from 1 mol FeOOH film, which is in agreement with the results of EQCM experiments. The fact that the discharge-specific capacity is slightly higher than the charge-specific capacity can be explained by the reduction of PC at a lower potential [24].

Figure 8 shows the cycle performance of FeOOH film prepared at the potential of  $-0.50 \text{ V}$  vs. Ag/AgCl in 1 M LiClO<sub>4</sub>/PC + DME(1:1 by volume)electrolyte and specific capacity as a function of cycle number at a current rate of 0.5 C. It can be seen from Fig. 8 that the first 20 cycles are irreversible, and the following cycles are reversible. The irreversible loss of specific capacity can be attributed to the formation of SEI layer [25], and the adsorption/desorption of some solvent molecules on the surface of FeOOH film. The FeOOH film maintains a specific capacity of about  $300 \text{ mAh g}^{-1}$  at the end of 170 cycles, which approximately equals the theoretical specific capacity of FeOOH given by reaction (4). This means that the lithiation and delithiation of FeOOH film are in a balance state. The results shown in Fig. 8 prove that the FeOOH film has a good electrochemical cycle ability in 1 M LiClO<sub>4</sub>/PC + DME (1:1 by volume) electrolyte.

### Conclusions

The composition of the film prepared by the electrodepositing on a gold film-coated electrode in Na<sub>2</sub>FeO<sub>4</sub> solution in the potential range of 0.18 to  $-0.57 \text{ V}$  vs. Ag/AgCl is FeOOH, and the measured mpe of FeOOH film in 1 M LiClO<sub>4</sub>/PC + DME(1:1 by volume) electrolyte during the charge/discharge process is close to the theoretical value in the potential range of 2.0–3.0 V, which corresponds to the extraction/intercalation of 1 mol lithium ions in 1 mol FeOOH. The FeOOH film exhibits a good cycle performance in 1 M LiClO<sub>4</sub>/PC + DME (1:1 by volume) electrolyte, and it maintains a specific capacity of about  $300 \text{ mAh g}^{-1}$  at the end of 170 cycles.



**Fig. 8** Cyclic performance of FeOOH film in 1 M LiClO<sub>4</sub>/PC + DME (1:1 by volume) electrolyte at a current rate of 0.5 C



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## References

1. Licht S, Wang BH, Gosh S (1999) *Science* 285:1039–1042
2. Licht S, Wang BH, Gosh S, Li J, Naschitz V (1999) *Electrochim Commun* 1:522–526
3. Walz KA, Suyama AN, Suyama WE, Sene JJ, Zeltner WA, Armacanqui EM, Roszkowski AJ, Anderson MA (2004) *J Power Sources* 134:318–323
4. Yu XW, Licht S (2007) *Electrochim Acta* 52:8138–8143
5. Koltypin M, Licht S, Nowik I, Vered RT, Levi E, Gofer Y, Aurbach D (2006) *J Electrochem Soc* 153:A32–A41
6. Licht S, Wang BH (2000) *Electrochim Solid State Lett* 3:209–212
7. Vered RT, Rozen D, Licht S (2003) *J Electrochem Soc* 150: A1671–A1675
8. Yu XW, Licht S (2007) *J Power Sources* 171:1010–1022
9. Licht S, Alwis CD (2006) *J Phys Chem B* 110:12394–12403
10. Yu XW, Licht S (2008) *J Appl Electrochem* 38:731–742
11. Licht S, Vered RT (2004) *Chem Commun* 6:628–629
12. Larramona G, Gutierrez C (1989) *J Electrochem Soc* 136:2171–2178
13. Buttry DA, Ward MD (1992) *Chem Rev* 92:1355–1379
14. Chen SL, Wu BL, Cha CS (1996) *J Electroanal Chem* 416:53–59
15. Kwon K, Evans JW (2004) *Electrochim Acta* 49:867–872
16. Uhm S, Yun Y, Tak Y, Lee J (2005) *Electrochim Commun* 7:1375–1379
17. Pech D, Brousse T, Bélanger D, Guay D (2009) *Electrochim Acta* 54:7382–7388
18. Bueno PR, Faria RC, Bulhões LOS (2005) *Solid State Ion* 176:1175–1180
19. Nishizawa M, Uchiyama T, Itoh T, Abe T, Uchida I (1999) *Langmuir* 15:4949–4951
20. Li JT, Chen SR, Fan XY, Huang L, Sun SG (2007) *Langmuir* 23:13174–13180
21. Morita M, Kishimoto A, Yoshimot N, Egashira M (2006) *Res Chem Intermed* 32:523–532
22. Amine K, Yasuda H, Yamachi M (1999) *J Power Sources* 81:221–223
23. Aurbach D, Moshkovich M, Cohen Y, Schechter A (1999) *Langmuir* 15:2947–2960
24. Aurbach D, Darouxa M, Faguy P, Yeager E (1991) *J Electroanal Chem* 297:225–244
25. Wang FM, Cheng HM, Wu HC, Chu SY, Cheng CS, Yang CR (2009) *Electrochim Acta* 54:3344–3351