

Short communication

## Zirconia coating stabilized super-iron alkaline cathodes

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### Abstract

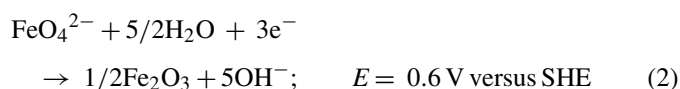
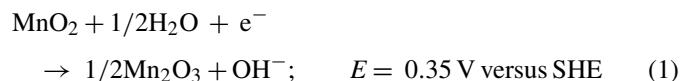
A low-level zirconia coating significantly stabilizes high energy alkaline super-iron cathodes, and improves the energy storage capacity of super-iron batteries. Zirconia coating is derived from  $ZrCl_4$  in an organic medium through the conversion of  $ZrCl_4$  to  $ZrO_2$ . In alkaline battery system,  $ZrO_2$  provides an intact shield for the cathode materials and the hydroxide shuttle through the coating sustains alkaline cathode redox chemistry. Most super-iron cathodes are solid-state stable, such as  $K_2FeO_4$  and  $Cs_2FeO_4$ , but tend to be passivated in alkaline electrolyte due to the formation of Fe(III) over layer. Zirconia coating effectively enhances the stability of these super-iron cathodes. However, for solid-state unstable super-iron cathode (e.g.  $BaFeO_4$ ), only a little stabilization effect of zirconia coating is observed.

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**Keywords:** Super-iron battery; Zirconia coating; Stabilization; Alkaline; Energy storage

### 1. Introduction

$MnO_2/Zn$  alkaline battery has been developed for over a century and is still playing a dominant share in the primary battery market because of its appropriate performance and low cost. However, it is well known that the storage capacity of this battery is limited by the charge capacity of  $MnO_2$  cathode ( $308 \text{ mAh g}^{-1}$ ), compared to that of Zn anode ( $820 \text{ mAh g}^{-1}$ ). Further energy storage improvements for the alkaline primary battery will be based on energetic alternatives to the  $MnO_2$ . Increases in cathodic energy storage can be based on both multiple electron transfer and more positive cathodic redox potentials. Super-iron batteries based on a class of unusual Fe(VI) compounds as the alkaline cathodes have been introduced and systemically studied in the past few years [1–5]. Compared with conventional  $MnO_2$  alkaline cathode (described Eqs. (1) and (2)), super-iron cathodes exhibit more positive electrochemical potential, sustain multi-electron ( $3e^-$ ) charge transfer and higher charge capacity.



So far, quite a few super-iron compounds have been successfully synthesized and studied as the cathodes for alkaline batteries. Among the super-iron cathodes,  $K_2FeO_4$  has been paid the most emphasis during the past few years due to its higher solid-state stability ( $<0.1\%$  decomposition/year) and higher intrinsic  $3e^-$  capacity ( $406 \text{ mAh g}^{-1}$ ) [1]. Most super-iron cathodes are solid-state stable, such as  $K_2FeO_4$  and  $Cs_2FeO_4$  [1,6]. However, in alkaline battery system, Fe(VI) cathodes tend to be passivated upon storage, by the formation of Fe(III) over layer [7–9]. While the bulk Fe(VI) remains active, but the overlayer passivates the cathode towards further discharge [9].

Due to its extreme stability in a wide temperature and environment range, zirconia has been used as a protective coating for a variety of materials [10,11], particularly in alkaline aqueous medium, zirconia could be attractive as it is practically insoluble ( $K_{sp} = 8 \times 10^{-52}$ ) and stable [12]. Typical zirconia deposition methods such as spray pyrolysis, plasma deposition, and colloidal deposition tend to deactivate or only partially cover electroactive surfaces [10,11,13]. In this paper, we introduce a novel  $ZrO_2$  coating methodology. The coating is obtained from an organic soluble zirconium salt,  $ZrCl_4$ , in the non-aqueous

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medium. Formation mechanism and performance of this coating, as well as its protection mechanism for  $K_2FeO_4$ ,  $Cs_2FeO_4$  and  $BaFeO_4$  super-iron cathodes are presented.

## 2. Experimental

Preparation and analysis of  $K_2FeO_4$  has been detailed elsewhere [14,15].  $K_2FeO_4$  of 97–98.5% is prepared according to



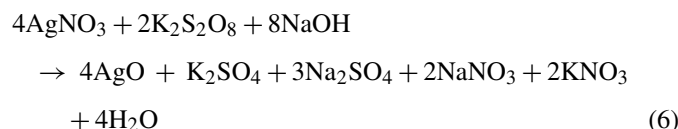
The dried  $K_2FeO_4$  product is stable in time, and may be used for other Fe(VI) salts (e.g.  $BaFeO_4$  and  $Cs_2FeO_4$ ) synthesis directly or after storage. Synthesis of  $BaFeO_4$  was detailed in Ref. [16] in accord with the reaction:



The  $Cs_2FeO_4$  was synthesized from  $K_2FeO_4$  by the driving formation via a hydroxide reaction in the  $CsOH$  solution [6]:



$AgO$  is prepared by standard methods [7] (the reaction at 85 °C of an alkaline  $AgNO_3$  solution with  $K_2S_2O_8$ ) in accord with



A typical 1%  $ZrO_2$  coating on  $MFeO_4$  ( $M=K_2, Cs_2, Ba$ ) is prepared as: 8 mg  $ZrCl_4$  (AR grade, ACROS®) is dissolved in 8 ml ether (Fisher®), and stirred with 0.8 g solid (insoluble)  $MFeO_4$  in the air for 30 min, followed by vertex suction, then vacuum removal of the remaining organic solvent, and drying overnight. Other percentage coating is prepared as the same way by adjusting the ratio of  $ZrCl_4$  and  $MFeO_4$ .

Analysis of the coating is performed with attenuated total reflectance Fourier transform infrared (ATR/FT-IR) spectrometry (Nicolet 4700), in which the powder sample (coated material) is compressed to a thin pellet and pressed firmly onto a Smart Orbit® (Thermo Electron Corporation) diamond crystal.

Performance and electrochemical enhancement of the zirconia coating is studied through preparation of button cells with

coated or uncoated cathode materials. Cathodes shown are composed of 20 mAh of  $K_2FeO_4$  or  $Cs_2FeO_4$  or  $BaFeO_4$  (coated or uncoated), with graphite as a conductor (1  $\mu$ m graphite, Leico Industries Inc.). Saturated KOH is used as the electrolyte, and the metal hydride anode is as removed from a Powerstream® Ni-MH button cell. Cells are discharged at a constant load of 3000  $\Omega$ . Cells potential variation over time is recorded via LabView Acquisition on a PC, and the cumulative discharge determined by subsequent integration. The coulombic efficiency is then determined as the percent storage capacity of the fixed, packed intrinsic capacity.

## 3. Results and discussion

### 3.1. Formation and analysis of $ZrO_2$ coating

Deposition of zirconia coating over a variety of super-iron salts is accomplished via a dissolved zirconium salt in an organic solvent which is mixed in a slurry/suspended powder solution formed with the insoluble super-iron salts. The solvent is removed by vacuum, with a zirconia overlayer on the salts. This zirconia coating methodology is based on a phenomenon in experimental chemistry and our experience [3]: that various possible transitional metal salts can be highly soluble in organic solvents, and are capable of forming a thin overlayer coating on the solid materials presented as insoluble particles in such an organic medium. Generally, transition metal compound cathode materials are insoluble in a wide range of organic solvents. Super-iron cathodes have been proved to be insoluble in variety of organic solvents, including the light molecule, low boiling point solvents and a series of solvents conductive to studies of lithium electrochemistry [2].  $ZrCl_4$ ,  $ZrOCl_2$ ,  $ZrI_4$ ,  $ZrOI_2$ , and  $Zr(NO_3)_4$ , all dissolve in ether and/or alcohol [17]. Zirconium chloride ( $ZrCl_4$ ) is used for the coating preparation in this paper. A variety of common, low boiling point solvents including, methanol, ethanol, acetone and ether, etc., have been studied as the organic medium for the formation of zirconia coating on the super-iron cathodes. Of these solvents, ether is finally chosen due to its facile evaporation (BP = 34 °C),  $ZrCl_4$  solubility, and no reaction or solubility with the super-iron cathode materials. Deposition parameters for a zirconia overlayer on  $K_2FeO_4$  are studied in detail, and the results are summarized in Fig. 1 ( $K_2FeO_4$  is used as the example). 0.3–5 wt% zirconia coating can be prepared through mixing 0.3–5 wt%  $ZrCl_4$

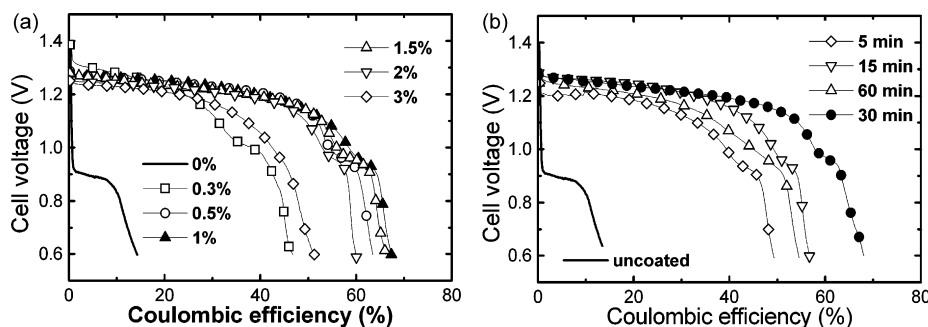
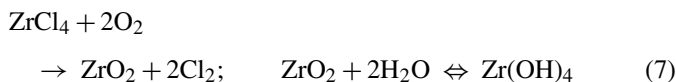


Fig. 1. Effects of coating amount (a) and coating time (b) on the stability of  $K_2FeO_4$  super-iron cathode.

with the remaining percentage of  $K_2FeO_4$  in ether media. The level of coating (% by weight) is important. Too high a coating thickness will diminish the conductivity of  $K_2FeO_4$  composite and thereby decrease its effectiveness as a cathode, whereas, too thin a coating is insufficient to cover the  $K_2FeO_4$  particle surface. One percent zirconia (to  $K_2FeO_4$ ) coating is observed to have the best effect on the performance of coated  $K_2FeO_4$  material (Fig. 1a). The coating time (stirring time of the slurry) is also significant. Time is required for a sufficient conversion from  $ZrCl_4$  to  $ZrO_2$ , although too long a time in the slurry can allow initiation of decomposition of some of the  $K_2FeO_4$ . The optimal coating time is observed to be half an hour (Fig. 1b). As a summary, 1% coating, 30 min stirring the  $ZrCl_4/MFeO_4$ /ether mixture at the room temperature are shown to have the best effect on the coating properties. Subsequent solvent removal including a quick vertex suction followed by a long-time vacuum drying (overnight) is also important for the coating formation.

ATR/FT-IR spectra of uncoated and 5 wt% zirconia coated  $K_2FeO_4$ ,  $Cs_2FeO_4$  as well as  $BaFeO_4$  cathode materials are shown in Fig. 2. Pure  $ZrO_2$  is also prepared (as a colloid without the cathode salt) for comparison. In ATR/FT-IR spectra of zirconia coated super-iron cathodes, the prominent  $1608\text{ cm}^{-1}$  peak of the original  $ZrCl_4$  fully disappears (not shown), and as seen in Fig. 2, new  $1396$  and  $1548\text{ cm}^{-1}$  peaks on the coated material coincides with the absorption spectra of pure  $ZrO_2/Zr(OH)_4$  depending on extent of hydration [18], which suggests that during coating formation, the zirconium chloride salt overlayer undergoes rapid spontaneous conversion to zirconia, consistent with the reaction [9]:



As noted in Fig. 2, on each super-iron cathode, a 5 wt% zirconia coating is prepared for the ATR/FT-IR analysis in order to

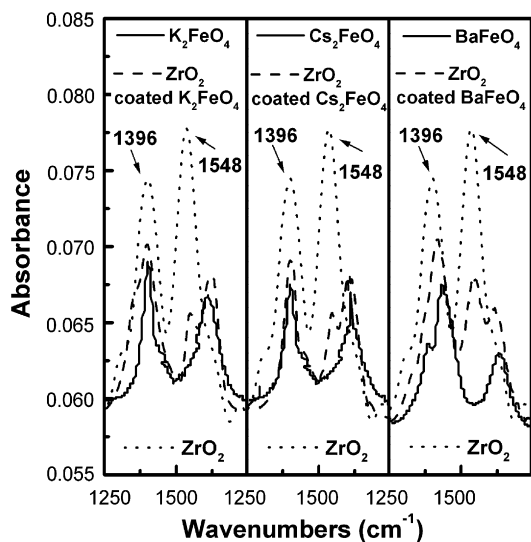


Fig. 2. IR absorption spectra of  $ZrO_2$  coated and uncoated cathode materials  $K_2FeO_4$ ,  $Cs_2FeO_4$  and  $BaFeO_4$ . Spectra are obtained by attenuated total reflectance Fourier transform infrared (ATR/FT-IR) spectrometry. Spectra of 5% coating included for emphasis.

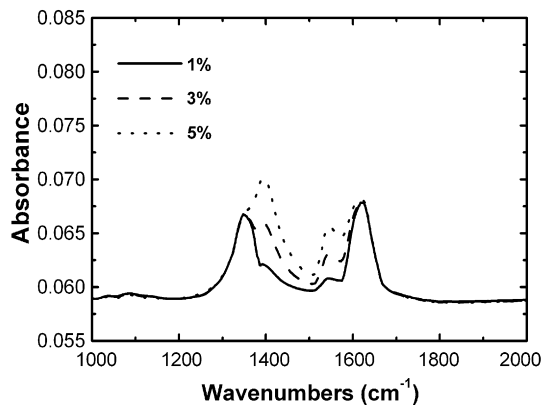


Fig. 3. ATR/FT-IR absorption spectra of  $K_2FeO_4$  cathode coated with 1%, 3% and 5% zirconia overlayer.

obtain obvious zirconia absorption peaks. Less percentage coatings also exhibit evident, but proportionally smaller,  $1396$  and  $1548\text{ cm}^{-1}$  peaks. This is demonstrated with  $K_2FeO_4$  cathode that is coated with 1% and 3% zirconia coating, as shown in Fig. 3.

### 3.2. Stabilization effect of zirconia coating on $K_2FeO_4$ , $Cs_2FeO_4$ and $BaFeO_4$ super-iron cathodes

Super iron batteries, utilizing a class of Fe(VI) compounds as the cathodes have high alkaline intrinsic capacities [1]. Among the super-iron cathodes, high purity of  $K_2FeO_4$ ,  $BaFeO_4$  and  $Cs_2FeO_4$  are readily synthesized. Physical and electrochemical characteristics of these three Fe(VI) salts are compared in Table 1.

In these super-iron cathodes,  $K_2FeO_4$  is particularly robust. Long-term (over 1 year) stability of this super-iron salt is proved:  $K_2FeO_4$  appears to be stable whether sealed under dry  $N_2$  or sealed in air, and is also stable under acetonitrile (and a variety of other organic solvents).  $Cs_2FeO_4$ , which is synthesized from  $K_2FeO_4$ , is also stable in the solid state while storing in the dry air or inert gas environment [6]. However, solid-state stability of the chemically synthesized  $BaFeO_4$  is much lower than that of  $K_2FeO_4$  and  $Cs_2FeO_4$ , especially for the chemically synthesized  $BaFeO_4$  salt [19].

As seen in Table 1, cathodic charge capacity of  $K_2FeO_4$  is higher than pure  $BaFeO_4$  and  $Cs_2FeO_4$ , but the rate of charge transfer of  $BaFeO_4$  is higher. Whereas  $K_2FeO_4$  and  $Cs_2FeO_4$  are stable under dry storage, passivation of these two salts is problematic upon storage in an alkaline battery. As seen in Fig. 4, the fresh pure  $K_2FeO_4$ ,  $BaFeO_4$  and  $Cs_2FeO_4$  cells discharge

Table 1  
Physical and electrochemical property comparison of high purity  $K_2FeO_4$ ,  $BaFeO_4$  and  $Cs_2FeO_4$  super-iron salts

	$K_2FeO_4$	$BaFeO_4$	$Cs_2FeO_4$
Solid stability	Good	Poor	Good
Intrinsic capacity ( $\text{mAh g}^{-1}$ )	406	313	209
Rate discharge	Low	High	Low

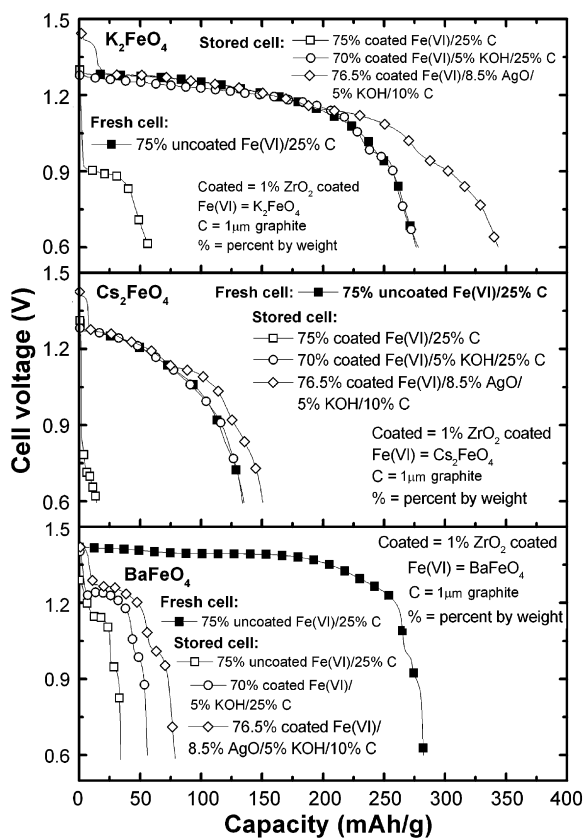


Fig. 4. Discharge capacity of  $K_2FeO_4$ ,  $Cs_2FeO_4$  and  $BaFeO_4$  (uncoated or coated, and their composite)—MH button cells fresh and after 7 days storage.

well, but the capacity decreases by an order of magnitude after 7 days of storage for each of these three cathodes.

In our recent studies, we have reported a low-level  $ZrO_2$  coating for the passivation protection of variety of alkaline cathodes and anodes [9,20].  $K_2FeO_4$  and  $KIO_4$  cathodes as well as  $TiB_2$  and  $VB_2$  anodes are effectively protected by the presence of a low-level  $ZrO_2$  coating. As also shown in Fig. 4, with 1% zirconia coating, capacity of  $K_2FeO_4$  and  $Cs_2FeO_4$  is retained after 7 days storage, however, capacity retention of  $BaFeO_4$  cathode is not significantly improved by this zirconia modification. The reason that caused this difference is proposed: in the  $BaFeO_4$  cathode case, the capacity loss is attributed to the chemical decomposition of this barium super-iron salt due to its chemically instability. Capacity loss of  $K_2FeO_4$  and  $Cs_2FeO_4$  is different, while the bulk Fe(VI) remains active, but the discharge product, Fe(III) overlayer passivates the alkaline cathode towards further discharge. Fe(VI) alkaline passivation of  $K_2FeO_4$  and  $Cs_2FeO_4$  can be suppressed through this zirconia modification. However, this zirconia coating has only a little effect on the chemical decomposition of  $BaFeO_4$ .

We have previously demonstrated the silver mediation of Fe(VI) charge transfer. A  $AgO/K_2FeO_4$  composite cathode provides a step toward an environmentally benign alkaline cathode with power and storage characteristics superior to the widely used conventional  $MnO_2$  cathode. As seen in Fig. 4, a low-level  $AgO$  additive to the coated  $K_2FeO_4$  and  $Cs_2FeO_4$  cathodes, not only facilitates charge transfer, sustaining an effective dis-

charge with a smaller conducting support (10%, rather than 25% graphite), but as seen in the figure yields an even greater discharge capacity than the uncoated, fresh  $K_2FeO_4$  and  $Cs_2FeO_4$ . The initial small 1.4 V voltage plateau evident in Fig. 4 for the  $MFeO_4/AgO$  composite cathode is largely due to the  $Ag(II \Rightarrow I)$  reduction of the added  $AgO$  [7,9].

Generally, zirconia is a type of ceramics material, and is extremely stable in a wide range of environment, even at high temperature. Practical stability of zirconia in alkaline medium effectively protects the super-iron cathodes in potassium hydroxide electrolyte from passivation. Stabilized zirconia has been used as a pH sensor for high temperature aqueous systems for a long time [21]. The hydrated zirconia,  $Zr(OH)_4$  has long been known as an ion conductor which will readily exchange between solution phase hydroxide, phosphate, fluoride, and sulfate [22–25]. This way, in the zirconia coated super-iron cathode, the insoluble zirconia centers provide an intact shield, and a hydroxide shuttle is necessary to sustain alkaline cathode redox chemistry [9].

#### 4. Conclusions

A novel methodology of zirconia deposition over a variety of super-iron cathodes is introduced. The zirconia coating is derived from  $ZrCl_4$  through an organic medium (ether). FT-IR analysis suggests that during coating formation, the zirconium chloride salt undergoes a rapid spontaneous conversion to zirconia. A low level, 1% zirconia coating significantly stabilizes high energy alkaline super-iron cathodes, and improves the energy storage capacity of super-iron batteries. Solid stable super-iron cathodes,  $K_2FeO_4$ ,  $Cs_2FeO_4$  are effectively protected by the presence of this zirconia overlayer from the passivation in alkaline electrolyte. However, only a little stabilization effect is observed for the chemical decomposition of solid-state unstable cathode  $BaFeO_4$ . Charge transfer stabilization mechanism of zirconia is proposed: in the zirconia coated super-iron cathode, the insoluble zirconia centers provide an intact shield, and a hydroxide shuttle in the zirconia coating is necessary to sustain alkaline cathode redox chemistry.

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