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Review

Advances in Fe(VI) charge storage
Part I. Primary alkaline super-iron batteries

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Abstract

Recent advances in super-iron batteries, based on an unusual Fe(VI) cathodic charge storage, are presented. Fe(VI) cathodes that have been demonstrated in super-iron batteries include the synthesized Fe(VI) compound with three-electron cathodic charge capacity Na_2FeO_4, K_2FeO_4, Rb_2FeO_4, Cs_2FeO_4 (alkali Fe(VI) salts), alkali earth Fe(VI) salts $BaFeO_4$, $SrFeO_4$, and also a transition Fe(VI) salt Ag_2FeO_4 which exhibits a five-electron cathodic charge storage. This paper focus on the primary alkaline Fe(VI) charge storage in aqueous electrolyte systems. Primary alkaline super-iron batteries exhibit a higher capacity than conventional alkaline batteries. Configuration optimization, enhancement and mediation of Fe(VI) cathode charge transfer of primary Fe(VI) alkaline batteries are summarized. Composite Fe(VI)/Mn(IV or VII), Fe(VI)/Ag(II) and zirconia coating stabilized Fe(VI)/Ag(II) cathode alkaline batteries are also illustrated.

Keywords: Fe(VI); Charge storage; Super-iron battery; Primary; Alkaline electrolyte

Contents

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1. Introduction

Fe(VI) species have been known for over a century, although its chemistry remains relatively unexplored [1–3]. Fe(III) compounds had been explored both as cathode [4] and anode [5] materials in electrochemical storage cells, however, higher valent, greater charge capacity, iron salts had not been previously considered, and the fundamental solubility and stability constraints on higher valent iron chemistry were not well established. Indeed, the perception that Fe(VI) species were intrinsically unstable was incorrect [6]. Recently, cathodes incorporating hexavalent, Fe(VI), sustaining facile, energetic, cathodic charge transfer have been introduced [6–32]. Resources to prepare Fe(VI) salts are plentiful and clean. Iron is the second most abundant metal in the earth's core, and the Fe(VI) reduction product is non-toxic ferric oxide. Fe(VI) salts can exhibit substantially higher than conventional cathodic storage capacities [6–32]. Due to their highly oxidized iron basis, multiple electron transfer, and high intrinsic energy, it has been defined high oxidation state iron compounds as 'super-iron's and the new electrochemical storage cells containing them as 'super-iron' batteries [6].

Capacity, power, cost, and safety factors have led to the annual global use of approximately 6×10^{10} primary batteries, but further advances are limited by the low energy capacity of their cathodes. New higher capacity, environmentally benign and cost effect cathode materials are needed. International interest in Fe(VI) electrochemistry is growing, including research efforts in China, Canada, Europe, and Japan [33–36]. Favorable battery cathodes characteristics are low solubility, stability, facile charge transfer, and high charge capacity, and oxidative electrochemical potential. K_2FeO_4, prepared as described in Ref. [11], is particularly robust. So far, the controlled syntheses of a wide range of Fe(VI) salts have been probed [9,11–13,18,23,25], including a direct route for their electrochemical synthesis from iron metal [23].

This paper focuses on the recent advances in Fe(VI) charge storage in aqueous electrolyte systems and the primary alkaline super-iron batteries.

2. Fundamentals and charge storage advantages of primary alkaline super-iron batteries

In 1999, Licht's group introduced a class of batteries, referred to as super-iron batteries, containing a cathode utilizing a common material (iron) in an unusual (+6) valence state [6]. The cathode is based on abundant starting materials and is compatible with an alkaline electrolyte and zinc anode. Among the different types of aqueous primary batteries available on the market, the Zn–MnO_2 system possesses the dominant share for over a century because of its appropriate performance and low cost. The storage capacity of the aqueous MnO_2/Zn battery is limited by the charge capacity of MnO_2 (308 mAh g^{-1}), compared to that of Zn (820 mAh g^{-1}). Replacement of the MnO_2 cathodes in these cells with a more energetic cathode such as Fe(VI) compounds can substantially increase the energy storage capacity of these cells. For example, using the same zinc anode and electrolyte, Fe(VI) cathode batteries were shown to provide 50% more energy capacity than in conventional alkaline batteries [6].

2.1. Fundamentals of alkaline super-iron batteries

Using Fe(VI) compounds as charge storage materials is based on the three-electron reduction of Fe(VI) via Eq. (1) or Eq. (2) (as the anhydrous product), which represent energetic and high-capacity source of cathodic charge [6]:

$$FeO_4^{2-} + 3H_2O + 3e^- \rightarrow FeOOH + 5OH^- \quad (1)$$

$$FeO_4^{2-} + (5/2)H_2O + 3e^- \rightarrow (1/2)Fe_2O_3 + 5OH^-,$$
$$E = 0.5\text{–}0.65\ \text{V versus SHE} \quad (2)$$

So far, a class of Fe(VI) salts are successfully synthesized, include the alkali Fe(VI) salts (high purity K_2FeO_4, Cs_2FeO_4, Rb_2FeO_4 and $K_xNa_{(2-x)}FeO_4$, low purity Li_2FeO_4), high purity alkali earth Fe(VI) salts ($BaFeO_4$ and $SrFeO_4$) and a transition metal Fe(VI) salt (Ag_2FeO_4). Theoretical three-electron charge capacity of the Fe(VI) salts are determined as: 3 F MW^{-1}, from the salt molecular weight, MW(g mol^{-1}) and the Faraday constant (F = 96,485 coulomb mol^{-1} = 26,801 mAh mol^{-1}). Theoretical capacities of various alkali and alkali earth Fe(VI) salts are listed in Table 1.

Ag_2FeO_4 is of interest, as this Fe(VI) salt commands an intrinsic cathodic capacity that includes not only the three-electron Fe(VI) reduction, but also the single electron reduction of each of two Ag(I) (as shown in Eq. (3)), for at total 5 Faraday

Table 1
Theoretical three-electron charge capacities of various Fe(VI) salts

Fe(VI) salts	Theoretical capacity (mAh g^{-1})
Li_2FeO_4	601
Na_2FeO_4	485
K_2FeO_4	406
Rb_2FeO_4	276
Cs_2FeO_4	209
$SrFeO_4$	388
$BaFeO_4$	313