Short communication

Evaluation of SiO$_2$ and TiO$_2$ coated BaFeO$_4$ cathode materials for zinc alkaline and lithium non-aqueous primary batteries

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Abstract

Barium ferrate material was coated with nanoparticulate thin films of SiO$_2$ and TiO$_2$ using sol–gel techniques, and was evaluated for use in both zinc-alkaline and lithium non-aqueous batteries. Iron(VI) content was monitored for ferrate materials stored under dry conditions and wetted with KOH and LiPF$_6$ electrolytes. Coated barium ferrate demonstrated improved stability relative to uncoated BaFeO$_4$. SiO$_2$ coated materials do not appear to be useful for either zinc alkaline or lithium non-aqueous systems at this time. TiO$_2$ coated materials demonstrated poor shelf life in alkaline electrolyte, but provided somewhat more favorable results in the lithium cells.
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1. Introduction

The performance of portable electronic devices is typically limited by the energy density of their battery power sources. Salts of the ferrate anion (FeO$_4^{2-}$) were first proposed as novel cathode materials by Licht et al. [1]. Since this initial report, several studies have investigated the three-electron reduction of Fe(VI) to Fe(III) to evaluate the suitability of ferrate materials for both zinc alkaline and lithium non-aqueous batteries.

In an iron(VI) battery, the iron containing cathode is reduced from its ferrate(VI) state to the ferric(III) state gaining three electrons per mole of cathode material. Licht et al. have described numerous ferrate compounds used in batteries that display higher charge capacities than traditional cells employing manganese dioxide as a cathode material [2–4]. However, despite the potential superior performance of ferrate-based batteries, development of these materials has been slow due to their chemical instability.

Licht et al. [5] studied the stability of potassium ferrate under a range of storage conditions and demonstrated that it was quite stable at temperatures from −5 to 45 °C, exhibiting <1% loss per year at room temperature provided that the material did not come in contact with moisture. In contrast, barium ferrate has been shown to decompose rapidly at 25 °C, losing a third of its activity in only 2 weeks time [6]. The decomposition of BaFeO$_4$ was slowed by decreasing the storage temperature, but gradual losses were still observed even at −30 °C. Recently, Ayers and White [7] employed Mossbauer spectroscopy to study the decomposition of barium ferrate produced from wet aqueous methods, and reported that solid cathodes formed from both potassium and barium ferrate salts degraded rapidly when stored in alkaline cells flooded with concentrated KOH electrolyte.

Licht et al. [8] have also shown that BaFeO$_4$ decomposition is dependent on the method used to synthesize the iron(VI) salt. Barium ferrate produced using wet aqueous techniques exhibited an activity loss of 55%, whereas electrochemically synthesized barium ferrate lost only 16% when stored under identical conditions. Hydration, particle size, initial Fe(III) content, and the presence of trace metals were all implicated as factors affecting barium ferrate stability.

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We recently investigated the stabilization of $BaFeO_4$ materials using nanoporous silica coatings and documented the performance of these materials in zinc alkaline batteries [6]. In this communication, we report on further experimentation using silica (SiO_2) and titania (TiO_2) coatings for barium ferrate materials in both zinc alkaline and lithium non-aqueous batteries.

2. Experimental methods

2.1. Synthesis and characterization of materials

Potassium ferrate was synthesized using the wet chemical method of Schryer et al. [9] as modified by Delaude and Laszlo [10]. A further description of the ferrate synthesis method employed is included in our earlier work [6]. Silicon dioxide and titanium dioxide thin film coatings were applied to barium ferrate materials using aqueous sol–gel techniques developed in previous studies [6,11]. Colloidal suspensions of SiO_2 and TiO_2 were prepared by base catalyzed hydrolysis of tetraethylorthosilicate and titanium isopropoxide precursors (Aldrich), according to procedures described elsewhere [12,13]. The resulting colloidal suspensions were analyzed using a Zetasizer 3000 dynamic light scattering system (Malvern Instruments). The pH of the aqueous sol was adjusted by dialysis to a range of 8–10 prior to deposition in order to prevent acidic decomposition of the ferrate. After coating, the aqueous sol–gel ferrate suspension was centrifuged at 4000 rpm (Beckman Model J21-21M) for 10 min at a temperature of 20 °C to separate the majority of the water from the coated solids. After decanting, the coated ferrate was freeze-dried overnight (Virtis Benchtop Model 378284) to complete the drying process. Coating morphology and surface coverage were examined using a Schottky field emission scanning electron microscope (LEO Gemini 1530). An in-lens secondary electron detector was utilized with an accelerating voltage of 3 kV to provide high resolution surface images.

2.2. Determination of stability

Coated and uncoated $BaFeO_4$ samples were stored as dry solids under vacuum at room temperature and monitored over time to determine their stability. The ferrate materials were assayed using the alkaline solution chromite titration method [14] to determine the percent iron(VI) content as described in previous studies [6,15]. Solid ferrates were also wetted with solutions of 1 M $LiPF_6$ dissolved in 1:1 (w/w) ethylene carbonate/diethyl carbonate solvent (Merck LP-40) and with saturated KOH solution to investigate their stability in the presence of both non-aqueous lithium and alkaline electrolytes. To simulate the conditions inside of a cell, 3.0 g of solid material was placed in a small vial and mixed with 1.2 mL of electrolyte to create a moist paste. The vials were capped for storage and periodically sub-sampled to assess the stability of the wetted ferrate. Vials containing non-aqueous lithium electrolyte were stored in a dessicator to prevent contamination of the organic liquid with residual humidity. Since silica is soluble in alkaline solutions, the

stability of SiO_2 coated materials was evaluated for the lithium electrolyte only.

Solid ferrates stored under electrolytes required washing and drying before they could be assayed. A small quantity of the solid material was removed from the electrolyte and vacuum dried on a GF/A glass microfiber filter to remove most of the liquid. Small quantities of pentane (50 mL) and diethyl ether (20 mL) were used to wash any remaining electrolyte from the solid material via vacuum filtration. Before proceeding with the chromite assay, samples were transferred to a dessicator and vacuum dried overnight to remove any remaining solvent. To insure accuracy of the chromite assay, triple replicate titrations were performed simultaneously by three individuals for several subsets of the ferrate samples, and mean purity values were recorded. Standard deviations using the triple replicate technique were typically less than 2%.

2.3. Chronopotentiometry

Test batteries were assembled using CR2032 stainless steel coin cells (Hohsen). The cathode layer was prepared by mixing 70% Fe(VI) material with 15% acetylene black (Cabot) and 15% SFG-6 graphite (Timcal). The cathode mix was ground with a mortar and pestle to produce a homogeneous mixture, which was formed into a thin pellet using a hydraulic press held at 69 MPa for 10 s. Pressed cathodes typically contained about 15 mg of active ferrate material.

Cathodes for lithium cells were vacuum dried overnight at ambient temperature to insure removal of any adsorbed water before transferring to an argon filled controlled atmosphere (H_2O and O_2 <5 ppm) glove box (Vacuum Atmospheres). Lithium cells were constructed using a lithium foil anode (Aldrich), two layers of tri-layered polyethylene/polypropylene separator (Celgard 2325), and LP-40 electrolyte. Assembled cells were crimp sealed in the glove box prior to transferring to the laboratory environment to prevent contamination with air or humidity.

Alkaline cells were prepared using an excess of Zn/ZnO anode paste obtained from disassembled commercial D-cell batteries (Rayovac), two layers of alkaline separator paper (Rayovac), and saturated KOH electrolyte. To allow for venting, alkaline coin cells were not crimped shut, but rather were clamped using an insulated mounting device. Cell discharge measurements were performed using a VMP2/Z electrochemical workstation (Princeton Applied Research) with EC-Lab V9.15 software.

3. Results and discussion

3.1. Coating characterization

Dynamic light scattering measurements showed that the SiO_2 particle size was significantly smaller than that of the particles in the TiO_2 sol (see Fig. 1). Particle size distributions were roughly normally distributed with mean particle sizes of 1.2 nm for SiO_2 and 4.6 nm for TiO_2. SEM examination of the coated ferrate materials also revealed significant differences between the sil-
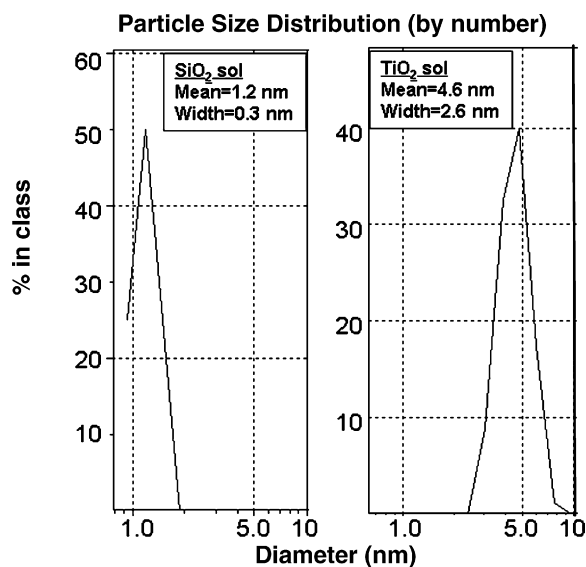
Fig. 1. Particle size distributions of silica and titania suspensions used for coating.

ica and titania sol–gel treatments (see Fig. 2). Silica coatings appeared very dense, and covered nearly the entire available ferrate surface. Titania coatings were not nearly as uniform. More than half of the ferrate surface appeared uncoated, and at magnifications of 200,000×, aggregates of primary TiO_2 particles could be observed that were distributed about the ferrate in a heterogeneous manner. Unfortunately, due to excessive charging of the materials, it was difficult to obtain digital images of good resolution at high magnification.

3.2. Ferrate stability

Fig. 3 shows the stability results for coated and uncoated barium ferrate materials that were stored under dry conditions and under KOH and lithium salt organic electrolytes at ambient temperature. The uncoated ferrate decomposed quickly under dry conditions losing about 20% of its Fe(VI) content in 7 days time. Previous studies had shown that SiO_2 coated barium ferrate was stable for several months when stored in air [6], and the new results show that TiO_2 coatings also appear to have a stabilizing effect relative to the uncoated control. The more rapid decomposition of the TiO_2 coated ferrate relative to the SiO_2 coated material is likely the result of the more irregular titania coating.

Ferrate decomposition was accelerated in the lithium salt organic electrolyte, and the uncoated barium ferrate lost over 75% of its Fe(VI) content in only 24 h. Although silica and titania coatings slowed this decomposition, after seven days, both of the coated specimens still displayed significant losses. Similar trends were observed for the uncoated and titania coated ferrate in the KOH electrolyte.

3.3. Zinc alkaline discharge results

Zinc alkaline TiO_2 coated ferrate cells discharged at $100\,mA\,g^{-1}$ realized only about 1/3 of their theoretical capacity ($\sim 311\,mAh\,g^{-1}$) before reaching a cutoff voltage of 1.0 V. This
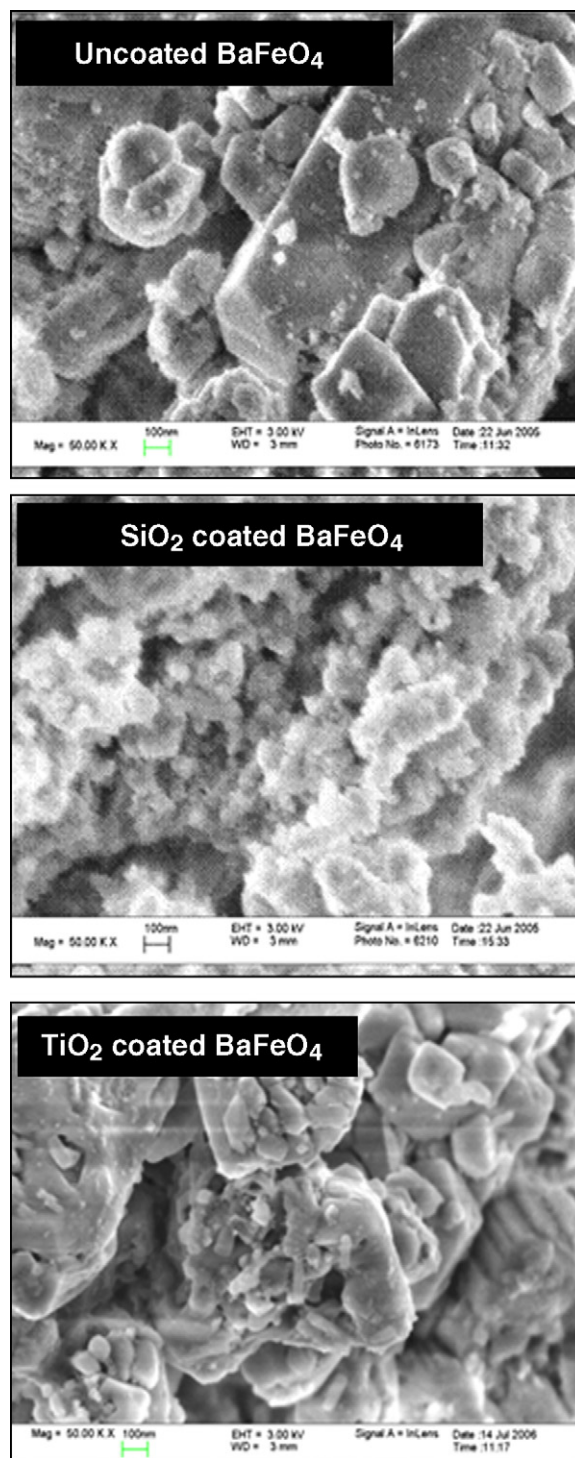

Fig. 2. SEM Images of coated ferrate materials.

capacity was slightly less than that previously reported for SiO_2 coated barium ferrate alkaline cells tested under similar conditions [6]. As would be expected, performance of the TiO_2 coated cells was improved by reducing the current to $50\,mA\,g^{-1}$, but even at the lower rate, typical discharge capacities were only 120 mAh/g. Representative discharge plots are shown in Fig. 4.

Unfortunately both coated and uncoated $BaFeO_4$ alkaline cells exhibited very poor shelf life when discharged after peri-

(a) dry storage

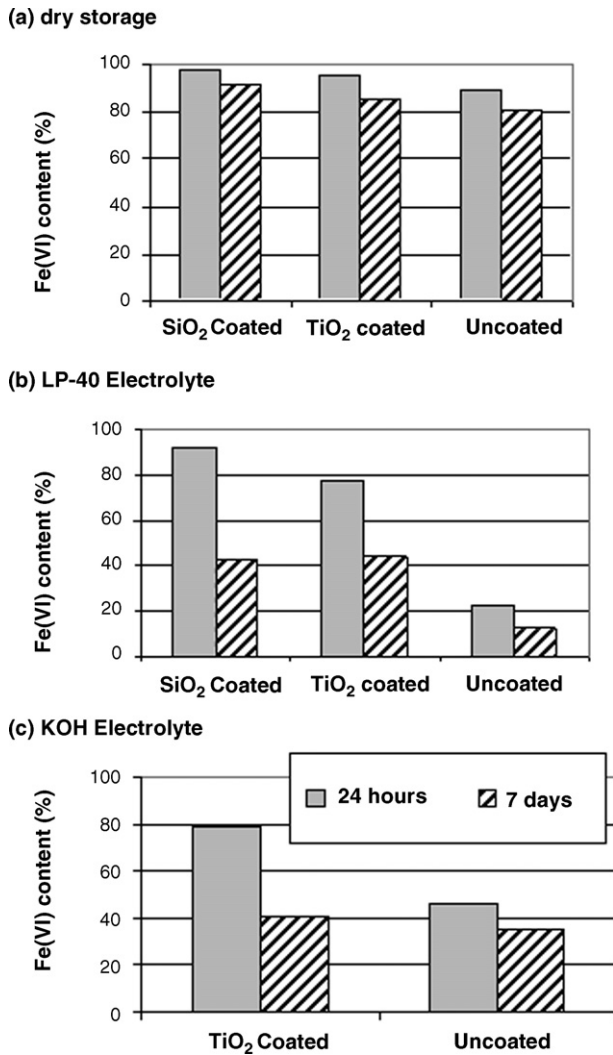## (b) LP-40 Electrolyte

(c) KOH Electrolyte

Fig. 3. Stability comparison of coated and uncoated barium ferrate materials at room temperature: (a) stored dry, (b) stored under lithium salt organic electrolyte and (c) stored under KOH electrolyte.

ods of 24 h or more. Other studies have documented the poor shelf life of alkaline ferrate cells [6,7] and commented on the formation of Fe(III) passivating-layers at the solid electrolyte interface of ferrate batteries. Visual inspection of dissected cells
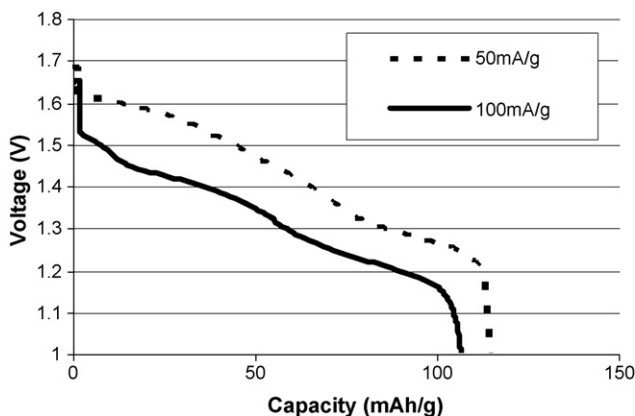
confirmed the appearance of rust colored material on the surfaces of both coated and uncoated cathodes when stored for 24 h. Based on these results, it appears that the initially porous sol–gel coating may become blocked with ferrate decomposition products that are formed in alkaline primary cells, thereby compromising cell performance.

3.4. Lithium non-aqueous discharge results

Uncoated barium ferrate material performed poorly in lithium primary cells. When discharged at $8\,mA\,g^{-1}$ to a cutoff of 1.0 V, cells had typical capacities of $\sim75\,mAh\,g^{-1}$. Higher discharge currents of 25 and $100\,mA\,g^{-1}$ further limited the discharge capacity of uncoated barium ferrate to ~35 and $\sim10\,mAh\,g^{-1}$, respectively. These discharge capacities are significantly lower than those reported by other authors for $BaFeO_4$ [16,17]. The lower discharge capacity that we observed is attributable in part to the higher applied discharge currents that we employed in this study. Additionally, the reduced capacity most likely indicates that some ferrate decomposition had already occured prior to the discharge testing of the lithium cells. Barium ferrate can decompose via evolution of oxygen gas [18], and it is possible that overnight vacuum drying and subsequent cell assembly may have further accelerated this process.

Significant differences were observed for SiO_2 and TiO_2 coated ferrate materials in lithium primary cells (see Fig. 5). TiO_2 coated cells exhibited a much larger capacity than the SiO_2 coated and the uncoated control materials. We attribute the poor SiO_2 performance to the small particle size and the density of the silica coatings. Assuming a random close packing of spherical particles, the sol–gel process results in the formation of pores that range between 0.2 and 0.5 nm in size for silica, compared to 0.7 to 1.9 nm in size for titania [19,20]. These pore sizes are significant, because viscosity and diffusion studies have shown that in carbonate electrolytes, the solvated Li^+ ion has an effective ionic radius of ~0.42 nm [21,22]. As a result, the ionic conductivity through the narrow pores of the silica coating would in many cases be prevented, and even for the larger pores would likely suffer severe kinetic limitations. By comparison,
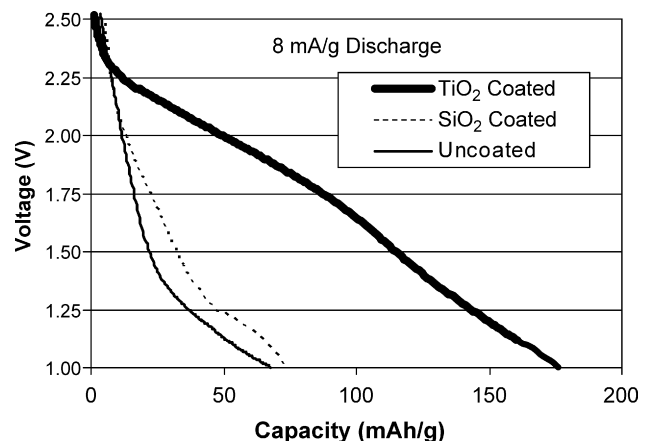

Fig. 4. Discharge curves for TiO_2 coated zinc alkaline BaFeO4 cells.

Fig. 5. Discharge curves for TiO_2 coated, SiO_2 coated, and uncoated lithium non-aqueous $BaFeO_4$ cells.

we attribute the superior TiO_2 discharge performance to a more open pore structure for the titania coatings that favors lithium ion transport.

If this hypothesis is correct, then further studies could explore parameters that might improve the performance of the sol–gel coatings for this application. If the TiO_2 coatings could be made more uniform (similar to that of the SiO_2) while retaining a suitable pore size distribution, it might be possible to create an improved stabilizing coating for barium ferrate that retained the Fe(VI) content of this material for extended periods of time. Alternatively, efforts could be made to synthesize SiO_2 sols having larger primary particle size to take advantage of the favorable evenly smooth coating behavior of this material while producing a coating with a larger mean pore size to better facilitate lithium ion transport.

4. Conclusion

$BaFeO_4$ decomposed rapidly when stored in both aqueous KOH and non-aqueous lithium salt organic electrolyte. The sol–gel coatings investigated in this study stabilized barium ferrate when stored in air, and to a lesser degree when stored in electrolyte. Although sol–gel coatings do not appear to be suitable for use in alkaline ferrate cells, the TiO_2 coatings provided some enhancement for barium ferrate used in lithium non-aqueous cells. However, TiO_2 coated $BaFeO_4$ still demonstrated inferior discharge capacity, voltage profile, and rate capability compared with other materials currently used in lithium primary batteries (e.g. manganese dioxide) [23]. It is possible that future exploration of sol–gel coating techniques might succeed in further improvement of barium ferrate for this application. Nonetheless, given the observed instability of barium ferrate in both alkaline and non-aqueous electrolyte, we conclude that this material is not suitable for commercialization as a primary battery cathode at this time.

Acknowledgements

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