The study of K_2FeO_4 (Fe^{6+}-super iron compound) as a cathode material for rechargeable lithium batteries

Maxim Koltypin [a], Stuart Licht [b], Ran Tel Vered [c], Vera Nashits [d], Doron Aurbach [a],*

[a] Bar-Ilan University, Department of Chemistry, Ramat-Gan 52900, Israel
[b] Department of Chemistry, University of Massachusetts Boston, 100 Morrissey Boulevard, Boston, MA 02125-3393, USA
[c] Department of Chemistry and Biochemistry, University of Texas at Austin, 1 University Station A5300, Austin, TX 78712-0165, USA.
[d] Faculty of Chemistry Technion, Haifa, 32000, Israel

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Abstract

In this work, we studied the possibility of using the Fe^{6+}-"super iron"-type compound, K_2FeO_4, as a potential cathode material for rechargeable Li batteries and its behavior in several types of non-aqueous solutions was investigated. Classical electrochemical techniques such as cyclic voltammetry and chronopotentiometry combined with photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Mössbauer spectroscopy, atomic adsorption (AA) and atomic emission (AE) have all been used in order to obtain a full picture of the electrochemical behavior for this compound.
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1. Introduction

In recent years, $MFeO_4$ (Fe^{+6} compounds, $M = K_2$, Ba, Sr, Cu) materials, denoted as "super iron compounds", were tested and developed as cathode materials in batteries by Licht et al. [1–6]. Some of these materials show a reversible behavior in alkaline aqueous solutions. Their synthesis, stability, basic structure and properties were studied very rigorously by the same group [4–6].

A major advantage of Fe(VI) compounds is their high theoretical capacity (406 and 313 mAh g^{-1} for K_2FeO_4 and $BaFeO_4$, respectively). K_2FeO_4 has a $BaSO_4$-type structure: an orthorhombic tetramolecular unit cell [7]. The theoretical capacity is calculated for the process of three-electron transfer in order to promote the reduction of the Fe(VI) to Fe(III). This means that three-lithium ions may be inserted to form compounds such as $Li_3K_2FeO_4$.

The above Fe(VI) oxides showed very interesting electrochemical behavior in aqueous media, such as high capacity

at relatively high current density when used as cathode materials in primary alkaline electrochemical cells [6]. The thermal stability of these compounds is still one of the most important limiting factors for their application as cathodes in commercial batteries. At room temperature, these "super iron" compounds show a reasonable stability and almost no solubility in alkaline aqueous solutions, as well as in organic ethereal and alkyl carbonate solutions. The goal of the present work was to study, as rigorously as possible, the electrochemical behavior of one of these compounds, namely K_2FeO_4, in non-aqueous solutions containing Li salts. It was especially important to investigate the possibility of using K_2FeO_4 as a cathode material for rechargeable Li batteries. Hence, it was very interesting to find out to what extent this compound reversibly inserts Li ions.

2. Experimental

As previously described in refs. [5,6], K_2FeO_4 was synthesized chemically and electrochemically. The purity of this compound was determined by a back titration analysis with solutions containing chromate ions. (The procedure for this

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tetrametric analysis of MFeO$_4$ compounds has already been published [4,5].) The purity of the K$_2$FeO$_4$ that we used for electrochemical and other measurements varied from 95 to 99%. For cyclic voltammetry measurements, we used coin-type cells (Type 2032, standard product from NRC Inc., Canada), in which metallic lithium foils were used as counter and reference electrodes. For galvanostatic cycling, we used either coin-type cells or flooded two-electrode cells (made of polyethylene and measured under highly pure Ar atmosphere, in hermetically sealed aluminum boxes). The electrodes measured in flooded cells were usually thicker than those in the coin-type cells, and were used for the XPS, XRD and Mössbauer measurements.

Composite "super iron" electrodes were prepared with 10, 20 and 30% (w/w) of carbon (acetylene black 99.9% pure from Alfa Aesar Inc. and/or KS6 synthetic graphite flakes from Timrex Inc.) and 10% polyvinyldene difluoride (PVdF), which were used as a binder. The electrolyte solutions included LiClO$_4$ (electrochemical grade, Tomiyama Chemicals), 1 M propylene carbonate (PC) (Merck KGaA, Li battery grade), mixtures of dimethoxy ethane (Aldrich, electrochemical grade) with PC, mixtures of ethylene carbonate (EC) with THF or dimethyl carbonate and DMC (Merck KGaA) or methyl-THF (Tomiyama Inc.). Other salts such as LiAsF$_6$, LiBF$_4$ or LiPF$_6$ were also used. We also used solutions containing NaClO$_4$ and Mg(ClO$_4$)$_2$ electrolytes. The coin-type and flooded cells were prepared under highly pure Ar atmosphere in VAC Inc. glove boxes.

Galvanostatic measurements were carried out using a Maccor, Model 2000 multi-channel battery analyzer. $C/10$ h rates were used (i.e., discharge or charge of the full theoretical capacity within 10 h) for thin, 2–9 mg cm^{-2} "super iron" cathodes and $C/50$ to $C/100$ h rates were applied for thick, 50–200 mg cm^{-2} composite cathodes that were used for XRD and Mössbauer measurements. Cyclic voltammetry was measured with a multi-channel potentiostat–galvanostat Model 1470 from Solartron Inc. XRD measurements were carried out using a Bruker Inc. D8 advanced XRD diffractometer in a θ–2θ configuration. Mössbauer measurements were carried out by Prof. Israel Novik at the Hebrew University, Jerusalem and are reported

in detail in parallel publications [8]. Some results are briefly mentioned herein in support of the electrochemical data.

Lithiated composite K$_2$FeO$_4$ cathodes ware analyzed by atomic absorption (AA) with a Perkin-Elmer 2380 atomic absorption spectrophotometer. The cathodes were dissolved in HNO$_3$/HCl concentrated acids solutions for element analysis by AA. We also carried out atomic emission (AE) measurements using a Gallenkamp Inc. flame analyzer. Surface element analysis by photoelectron spectroscopy and XPS measurements, was carried out using a system from Kratos Inc. (HS axis ultrahigh vacuum XPS spectrometer). For these measurements, we prepared electrodes without additives, in which the active mass was embedded in aluminum foil current collectors. The electrodes for the XPS measurements were removed from the cells under highly pure Ar atmosphere, washed with highly pure THF (Merck or Tomiyama) and transferred to the UHV–XPS system by a special home made transfer device, without being exposed to any atmospheric contaminants.

3. Results and discussion

Fig. 1 shows typical cyclic voltammograms of composite electrodes comprising K$_2$FeO$_4$, carbon black and PVdF (a) 80% active mass, 10% carbon and 10% binder; and (b) 70% active mass, 20% carbon and 10% binder in a PC–LiClO$_4$ solution. These voltammograms show that the K$_2$FeO$_4$ is electrochemically active. A reduction process is clearly seen in the 1.5–2.5 V (Li/Li$^+$) potential range, to which an oxidation process around 3–4 V corresponds. The broad peaks with the very large hysteresis between the peaks (1.5 V) means that the electrochemical process is complicated and suffers from severe kinetic limitations.

Fig. 2 shows typical chronopotentiograms of the electrodes in repeated galvanostatic cathodic and anodic polarization in an EC–PC 1:1/LiClO$_4$ 1 M solution. The sloping potential profile between 3 and 1.5 V during the cathodic processes and the sloping potential profiles in the range of 2.5–4 V during the anodic processes corresponds to the cyclic voltammetric response presented in Fig. 1. Element analysis of cycled electrodes using atomic absorption (see the
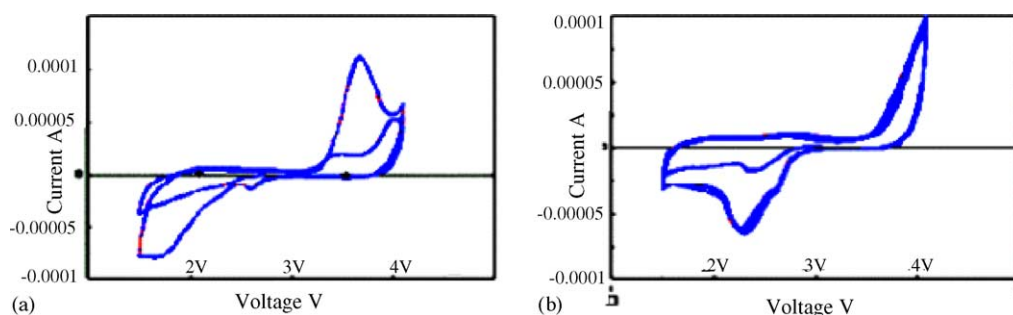

Fig. 1. Cyclic voltametry of K$_2$FeO$_4$ cathodes with different amount of added carbon: (a) with 20% carbon black and (b) with 10% carbon black, 1 M LiClO$_4$ in PC-based solution, 200 mV s^{-1}.
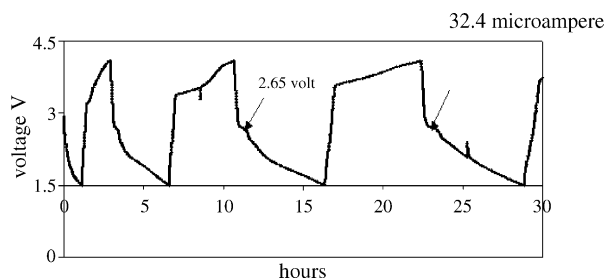
Fig. 2. Voltage profile of composite K_2FeO_4 composite electrodes during first galvanostatic cycling at (C/15) rate in EC–PC 1:1/1 M $LiClO_4$ solution. During the first cycles, the capacity increases from cycle to cycle (see text).

working procedures in Section 2) show that lithium is indeed inserted into the active mass in amounts corresponding to the charge measured. Anodic polarization does not remove all the lithium from the active mass. This finding also correlated with the charge measured during the anodic process that preceded the element analysis.

Hence, we can conclude that the electrochemical processes demonstrated in Figs. 1 and 2 indeed relate to the lithiation and delithiation of the electrodes.

XPS spectra showed the presence of lithium in the cathodes polarized to low potentials. We also discovered by XPS that electrodes that were polarized cathodically in alkyl carbonate solutions became covered by surface films comprising lithium carbonate as a component. It was impossible to determine the valence of iron from the XPS spectra. Fig. 3 shows curves of capacity versus the cycle number of K_2FeO_4 electrodes containing different amounts of carbon, as indicated. As seen in this figure, it takes the electrodes a few cycles to reach a maximal capacity close to the theoretical value ($\approx$350 mAh g^{-1}), depending on the electrode's composition. The capacity then fades from cycle to cycle and stabilizes at a low value (no more than one-third of the theoretical capacity). These electrodes could be cycled reversibly hundreds of times in the alkyl carbonate-based solutions, showing low ($\approx$100 mAh g^{-1}), but stable capacity.
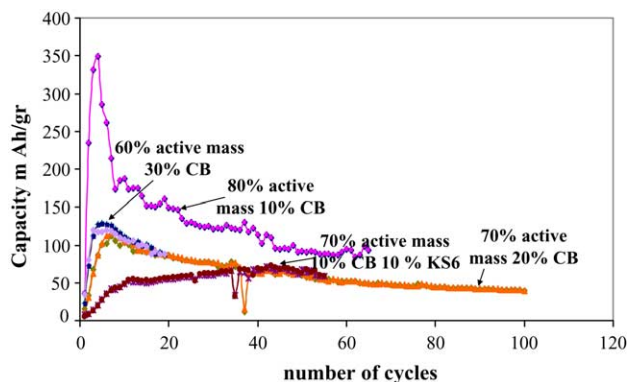

Fig. 3. Charge/discharge capacity vs. cycle number of K_2FeO_4 composite "super iron" cathode with different concentrations of carbon, as indicated. Galvanostatic cycling at C/15 rate in EC–PC 1:1/1 M $LiClO_4$.
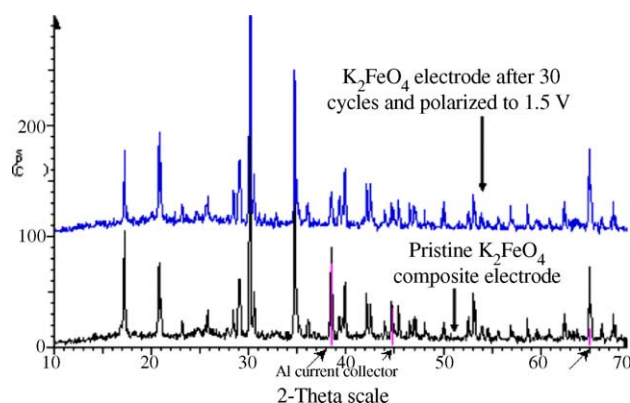

Fig. 4. XRD patterns of pristine K_2FeO_4 composite electrode and of the same electrode after 30 lithiation–delithiation, cycled at a relatively low capacity ($\sim$100 mAh g^{-1}) in $LiClO_4$ in PC–DME 1:1 solution.

Fig. 4 shows XRD patterns of a pristine K_2FeO_4 electrode and of this electrode after being cycled galvanostatically 30 times. The electrode was removed from the cell for these measurements after being polarized to 1.5 V (Li/Li$^+$). The patterns of the pristine electrode reflect its highly crystalline structure ($BaSO_4$ type, orthorhombic tetra molecular unit cell [7]). The patterns of the cycled electrodes contain the same peaks of the pristine electrode, but at a lower intensity. More rigorous XRD measurements of fully lithiated electrodes that reached a lithiation level close to the theoretical one ($\approx$3 Li per K_2FeO_4 molecule, $\sim$350 mAh g^{-1}) showed that the fully lithiated electrodes lost their crystalline structure, showing no XRD peaks. Their delithiation also produced material that showed no XRD peaks. Mössbauer spectroscopy (to be reported on elsewhere [8]) confirmed that lithiation of K_2FeO_4 changes the oxidation state of the iron from 6$^+$ to 3$^+$, and that delithiation of the reduced material produces an iron 6$^+$ compound. However, part of the Fe^{3+} compound remains in the delithiated material, and hence the process is not fully reversible.

Assembling all the above information leads to the conclusion that K_2FeO_4 does not intercalate with lithium, but rather undergoes a partially reversible redox process that reduces the iron in the compound from 6$^+$ to 3$^+$, and involves a reaction with Li ions as well. Their initial reduction process leads to an amorphization of the pristine materials, after which the redox process, which is partially reversible, takes place between amorphous phases. The most probable reaction that we can suggest is:

$$2K_2FeO_4 + 6e^- + 6Li^+ \leftrightharpoons 2K_2O + 3Li_2O + Fe_2O_3.$$
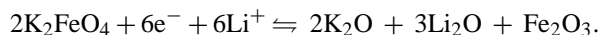
This reaction resemble to some extent the reversible reduction of oxides such as FeO or CoO in the presence of lithium ions to form the metal particles and Li_2O as was previously described by Tarascon and co-workers [9].

The fact that it takes a few cycles to reach the maximal capacity may be attributed to the poor impregnation of the active mass by the solution. Hence, the change in the phase structure during lithiation (amorphization) enables the solution to

reach the entire active mass. The process is then only partially reversible, probably due to the poor electronic and ionic conductivity of the amorphous phases involved in the processes.

4. Conclusion

As expected, K_2FeO_4 can be electrochemically reduced in non-aqueous Li salt solutions. This process involves lithiation and reduction of the iron from 6^+ to 3^+ states (confirmed by AA, Mössbauer spectroscopy and charge measurements in the electrochemical processes). This reduction process leads to an amorphization of the compounds involved (XRD). The process is only partially reversible. After a full lithiation is obtained (at a capacity close to the theoretical one), the process becomes only partially reversible. The electrodes can be cycled hundreds of times with a reversible capacity, which does not exceed one-third of the theoretical capacity. The fine electrochemical behavior of these electrodes (in terms of maximal capacity, capacity fading, the stable low capacity, etc.) is strongly dependent on their structure (thickness, amount of carbon added, compactness) and the electrolyte solution used.

It is clear that the process does not involve intercalation of lithium, but rather involves a redox reaction that completely changes the chemical composition and structure of the active mass. The fact that during prolonged cycling (voltammetric, galvanostatic) some reversibility is obtained encourages further study of these materials. It is quite possible that the low (but stable) capacity measured during prolonged cycling is due to poor transport properties (both electronic and ionic) of the active mass in its amorphous structure. It may be possible to improve these transport properties by the use of better and well-dispersed conductive additives.

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