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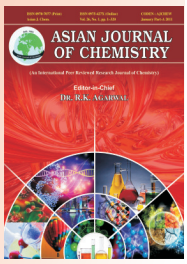

Discharge Behavior of Tungsten(VI) Oxide Cathodes in Medium-Temperature Lithium Batteries for Borehole Applications

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We have investigated the electrochemical properties of WO_3 and Li_2WO_4 used as cathode materials for medium-temperature (200-300 °C) lithium batteries coupled with binary and ternary nitrate eutectic electrolytes. Discharge tests are performed on the combinations of LiMgB/nitrate/tungsten (VI) oxide cells at a current density of 10 mA·cm^{-2}. In general, compared with Li_2WO_4 cathode, WO_3 presents multistep and more sloping voltage plateaux and much less capacities. Compared with binary $LiNO_3$-KNO_3 electrolyte, ternary $LiNO_3$-KNO_3-$CsNO_3$ electrolyte shows better kinetic activity. The highest cathode capacity of 397.09 mAh g^{-1} to a 1V cut-off appears in the LiMgB/$LiNO_3$-KNO_3/Li_2WO_4 cell at 200 °C. The compatibility research between tungsten (VI) oxides and nitrate eutectics indicates that no obvious exothermic reactions occur in the temperature range envisaged. The specific reaction mechanisms of the WO_3 and Li_2WO_4 cathodes are also preliminarily investigated by XRD method.

Keywords: Tungsten (VI) oxide cathodes, Medium-temperature lithium batteries, Discharge behavior, Borehole applications.

INTRODUCTION

Modified lithium/thionyl chloride batteries are widely used as power supplies for measurement while drilling (MWD) equipment in boreholes for geothermal, oil and gas exploration[1]. This energy supply system usually works with characteristics of low current, long life and a wide operating temperature range. However, due to the low decomposition temperature of $SOCl_2$ and high vapor pressure inside batteries at higher temperatures, this technology is strictly limited below 200 °C. The use of dewars above 200 °C expands the operating temperature range but also increases the cost of production simultaneously. So much attention has been paid to develop a new battery technology using low-temperature molten salt electrolytes in recent years[2]. After extensive material screening tests, nitrate-transition metal oxide combinations have been found to well meet the demand of practical work. The nitrate eutectics with relatively low melting points melt automatically by the use of the heat of boreholes, which can eliminate additional internal pyrotechnic and simplify cell structures tremendously. Also, a number of transition metal oxide cathodes are compatible with nitrates without any exothermic reaction between them in the operating temperature range, which are quite superior to the traditional sulphur-based cathodes in thermal batteries. The basic electrochemistry of nitrate-containing molten salt electrolytes and transition metal oxide cathodes has been widely studied by Miles[3-5]. Guidotti *et al.*[6,7] have reported the discharge behavior and applicability of the Ag_2CrO_4 and MnO_2 cathodes. These systems all show excellent performances in the envisaged work environment for boreholes.

WO_3 was used primarily as a cathode material in thermal batteries in the early 1950s coupled with Ca or Mg anodes[8], but due to its poor conductivity and reactivity with halide melts, this technology was quickly replaced by the Ca/$CaCrO_4$ system in the mid-1950s. In addition, there is almost no information in the open literature concerning the electrochemistry of the WO_3 as used in thermal batteries[9,10]. However, for the medium-temperature lithium batteries, nitrates rather than halides are used as electrolytes. Graphite can be added to improve the electrical conductivity effectively, so WO_3 is worth being reevaluating the feasibility as a cathode material in medium-temperature batteries. As is known that transition metal oxides generally have the disadvantages of low electrical conductivity and poor thermal stability. However, lithiation of them can produce both thermally stable and electronically conducting structures which will accept additional lithium ions during the reduction[11]. Here, we take tungsten (VI) oxide and lithiated tungsten (VI) oxide as our objects of study. Discharge behavior, reaction mechanism and compatibility with binary and ternary

nitrate salts will be discussed in detail. The ultimate goal is to study the electrochemistry of WO_3 and Li_2WO_4 and develop a proper medium-temperature lithium battery system.

EXPERIMENTAL

WO_3 and Li_2WO_4 from Strem Chemical Inc. and other starting materials from Sinopharm Chemical Reagent Co, Ltd were all of reagent grade with purity higher than 98.5 %. (Unless otherwise noted, all compositions are reported as weight percent). The LiMgB alloy anode (64 % Li, 4 % Mg and 32 % B) was prepared by ourselves. Anodes were obtained by punching disks (15.5 mm diameter, 0.09 g mass) from LiMgB foil (0.44 mm thickness). All salts were vacuum-dried at 100 °C overnight before use. The eutectic ratios of the $LiNO_3$-KNO_3 electrolyte (33.2 % $LiNO_3$, 66.8 % KNO_3) and $LiNO_3$-KNO_3-$CsNO_3$ electrolyte (21.43 % $LiNO_3$, 35.54 % KNO_3 and 43.03 % $CsNO_3$) were both weighed out and fused for 16 h at 300 °C. The catholytes were prepared by blending 70 % WO_3 or Li_2WO_4 with 20 % electrolyte and 10 % graphite, electrolyte and graphite were added necessarily to improve the ionic and electrical conductivity respectively. Then the mixture was vacuum-dried at 80 °C for 8 h to eliminate extra moisture.

Analysis of materials: To determine the compatibility between tungsten (VI) oxides and nitrate eutectics, simultaneous TGA/DSC was performed on a NETZSCH STA 449F3 thermal analyzer. The thermal analysis samples were sealed in an Al_2O_3 pan, the heating rate was 5 °C/min and the upper limit temperature was set as 350 °C. To identify reaction mechanisms of the two cathodes, XRD was performed on a Rigaku D/MAX-2200/PC diffractometer with CuK_α radiation, the scanning range was from 10° to 90° with a scanning speed of 4°/min.

Preparation of pellets for single cell tests: Experimental single cells consisted of a 0.09 g LiMgB pellet and a bilayer pellet consisting of 0.50 g each of depolarizer-electrolyte (DE) and electrolyte binder (EB) layers pressed at 222 MPa. Then the two pellets were sandwiched between stainless steel current collectors and put between heated plates in a glovebox under an atmosphere of high-purity argon (< 1 ppm each of water and oxygen). Mica insulations were used between single cells and heated plates to avoid any electrical contact. The discharge measurements were performed on an EG&G PARC Model 273A potentiostat/galvanostat controlled with the Model 270 software package in a temperature range of 200-300 °C. A steady-load of 18.9 mA (10 mA cm^{-2}) was used, which was adequate for the envisioned application[6]. The discharge process was terminated when the voltage dropped below 1 V.

RESULTS AND DISCUSSION

Thermal analyses: Thermal analysis was accomplished prior to high-temperature discharge tests to avoid any risks, especially runaway in batteries. Any cell combination containing intense exothermic reactions in the predetermined temperature range should be eliminated. The compatibility between two kinds of active cathodes and two kinds of nitrate eutectics was examined by TG/DSC analyses. The results are shown in Figs. 1a, b.

It can be seen from Fig. 1a that the four TG curves only present different levels of decline slightly, which most likely corresponds to the removing of moisture in the samples. As shown in Fig. 1b, there is only two endothermic peaks appear in DSC curves for the binary eutectic below 300 °C without any exothermic peak. The main peak at 135.1 °C is agreement with the melting point of the $LiNO_3$-KNO_3 eutectic (124.5 °C) but a little higher. The other weaker peak at 123.3 or 121.5 °C may result from the impurities in starting materials. With the increasing of temperature, fluctuation of curve begins to appear from 314.1 °C in the $LiNO_3$-KNO_3/WO_3 cell. However, there is no corresponding evidence in the TG curve of this combination as to exothermic reactions occur in this temperature range. The results associated with the ternary $LiNO_3$-KNO_3-$CsNO_3$ eutectic show that only a single endothermic peak appeared at 122 °C or 120.6 °C in DSC curses which corresponds to the melting point of the ternary eutectic (96 ± 2 °C)[12] but a little higher. TG curves also well ensure the safety of these two cell combinations below 350 °C.

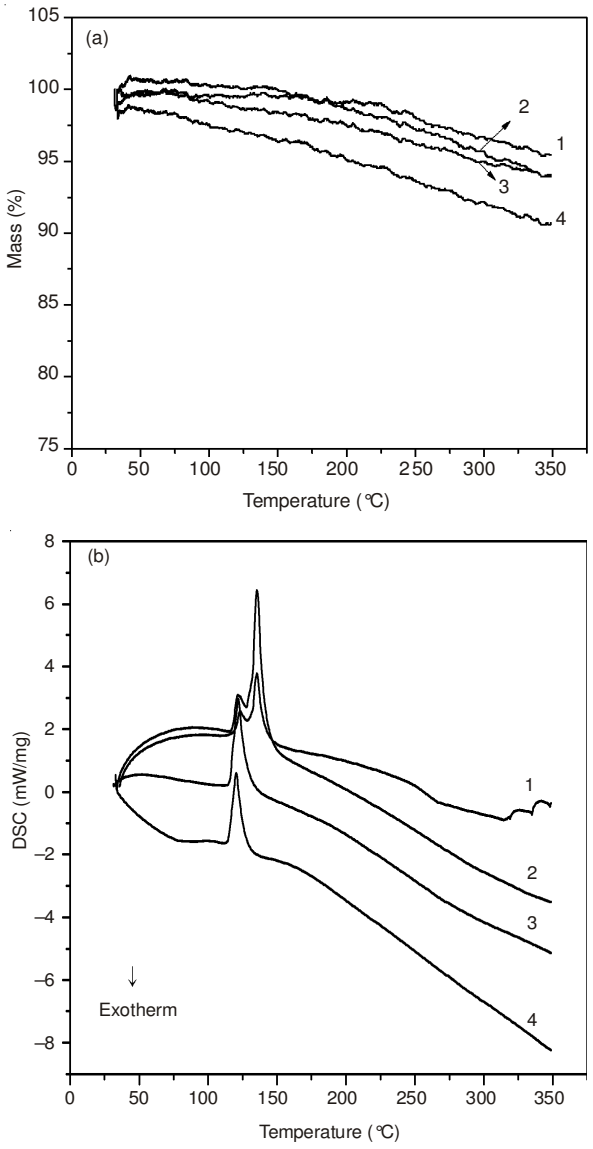

Fig. 1. TG and DSC curves of (1) WO_3 + binary eutectic, (2) Li_2WO_4 + binary eutectic, (3) WO_3 + ternary eutectic, (4) Li_2WO_4+ ternary eutectic

Single cell tests: The discharge curves obtained for WO_3 and Li_2WO_4 are presented in Figs. 2a and 2b, respectively at 200 and 300 °C coupled with the two eutectic electrolytes. As is shown in Figs. 2a and Table-1, the LiMgB/WO_3 cells each has an open-circuit voltage (OCV) of around 3.4 V. At a higher temperature of 300 °C, higher and more distinct voltage plateaux and much higher capacities are the major differences from the corresponding results at 200 °C. These improvements may attribute to the higher reaction activity of the WO_3 cathode at 300 °C. The two distinct voltage plateaux at 300 °C indicate a two-step redox reaction during discharge together with lithium intercalation. At each temperature, cells with ternary eutectic electrolyte usually perform better on the aspects of voltage plateau and discharge capacity than those with binary eutectic electrolyte. As the melting point of ternary $LiNO_3$-KNO_3-$CsNO_3$ eutectic is lower than that of the $LiNO_3$-KNO_3 eutectic, so higher kinetics is obtained in the ternary eutectic at the same temperature, which contributes to better electrochemical performance.

As is shown in Fig. 2b, only one distinct voltage plateau are presented in each LiMgB/Li_2WO_4 cell, which indicates that Li_2WO_4 goes through a one-step redox reaction. These cells have wider and steadier voltage plateaux and much higher capacities than those of the LiMgB/WO_3 cells. The highest cathode capacity of 397.09 mAh g^{-1} appears in the LiMgB/$LiNO_3$-KNO_3/Li_2WO_4 cell at 200 °C. Rather than WO_3, more simple lithium intercalation process occurs in Li_2WO_4 during discharge, which results to steadier plateaux. Frequent phase transitions resulting from multistep lithium intercalation occurred in WO_3 and other Li-free transition metal oxides affect the structural stability and then the electrochemical performance. Unlike the LiMgB/WO_3 cells, better properties are obtained at the lower temperature of 200 °C rather than 300 °C for the LiMgB/Li_2WO_4 cells. The increased self discharge in these cells at higher temperature is most likely responsible for it, which is similar with the Li (Al)/MnO_2 cells[7].

Phase structures analyses: As described earlier, the WO_3 cathode experiences a distinct two-step reaction process at 300 °C and a one-step reaction occurs in the Li_2WO_4 cathode at both 200 and 300 °C. XRD is used to detect the reaction products of WO_3 and Li_2WO_4 and then analyze the specific mechanisms of them. The partially discharged cathode layers are stripped from the LiMgB/$LiNO_3$-KNO_3-$CsNO_3$/WO_3 cell at 300 °C and the LiMgB/$LiNO_3$-KNO_3/Li_2WO_4 cell at 200 °C, respectively which have the highest capacities for each of the cathodes. XRD patterns of the partially discharged cathode layers are shown in Fig. 3.

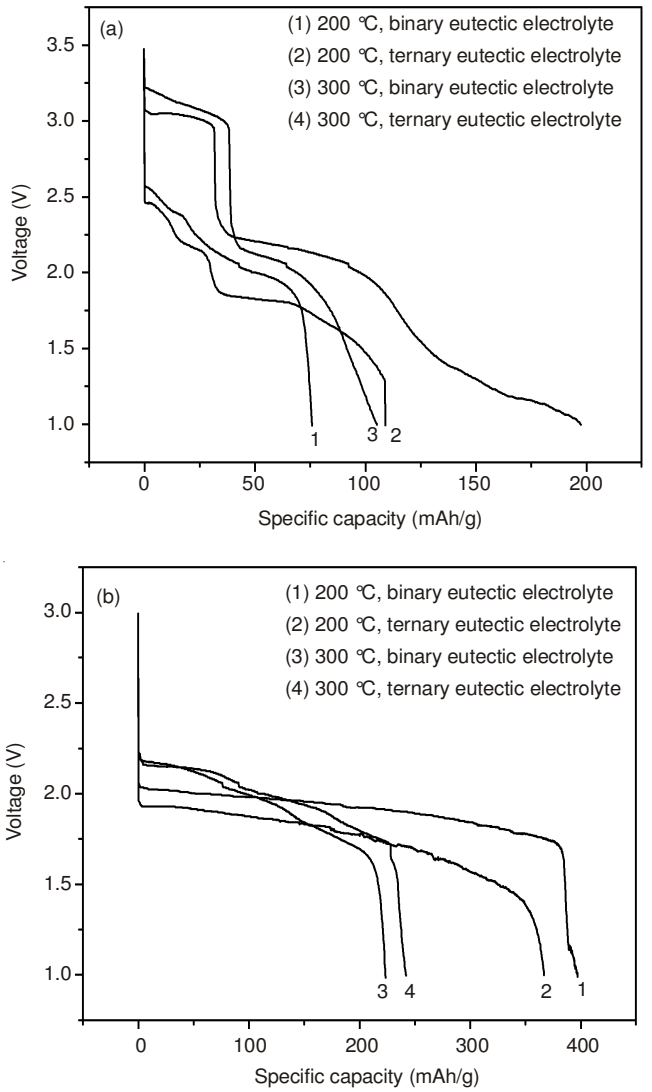

Fig. 2. Galvanostatic discharge profiles of (a) the LiMgB/WO_3 cells and (b) the LiMgB/Li_2WO_4 cells

When the WO_3 cathode is discharged to the end of the first voltage plateau, namely a 2.75V cut-off, besides the diffraction peaks of additives, the others are well in agreement with the JCPDS cards of $7Li_2WO_4{\cdot}4H_2O$ and WO_3. The crystal water most likely comes from moisture in surroundings during the testing process. And the existence of WO_3 indicates that not all the WO_3 is involved in the process of lithium intercalation reaction. Similar to the products of the first plateau, the diffraction peaks are in accordance with JCPDS cards of Li_2WO_4 and WO_3 for the WO_3 cathode discharged to a 1 V

TABLE-1
GALVANOSTATIC DISCHARGE RESULTS FOR THE WO_3 AND Li_2WO_4 CATHODES

Cell combination	Temperature (°C)	OCV (V)	Capacity to a 1V cut-off (mAh)	Energy density to a 1Vcut-off (mAh g^{-1}) cathode
$LiNO_3$-KNO_3/WO_3	200	3.411	27.18	77.66
	300	3.474	37.33	106.66
$LiNO_3$-KNO_3/Li_2WO_4	200	2.940	138.98	397.09
	300	2.679	80.59	230.26
$LiNO_3$-KNO_3-$CsNO_3$/WO_3	200	3.440	37.83	108.09
	300	3.377	69.81	199.46
$LiNO_3$-KNO_3-$CsNO_3$/Li_2WO_4	200	2.854	128.01	365.74
	300	2.994	87.27	249.34

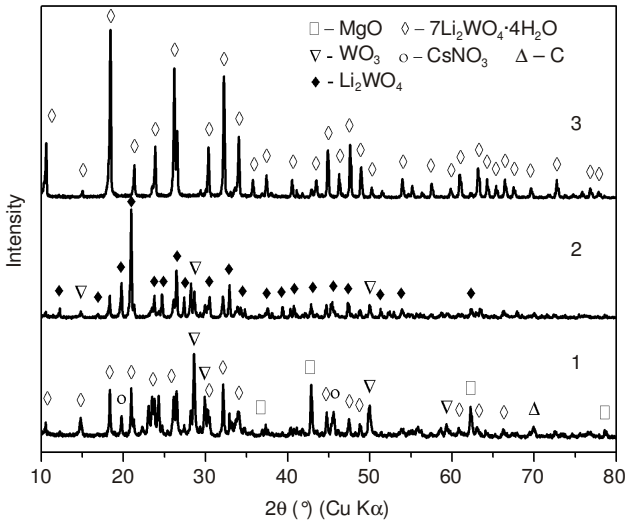

Fig. 3. X-ray diffractograms of the partially discharged cathode layers: (1) discharged WO_3 to a 2.75 V cut-off; (2) discharged WO_3 to a 1 V cut-off; (3) discharged Li_2WO_4 to a 1 V cut-off

cut-off. As the discharge process of WO_3 is together with lithium intercalation and lithium-poor and lithium-rich lithium tungstates share the similar XRD patterns, we conclude that WO_3 experiences a step-by-step lithium intercalation process on the two voltage plateaux and converts to Li_xWO_4 (the x value increases with the decrease of the voltage plateaux), as shown in eqn. 1. The increased oxygen is believed from the reduction of the NO_3^-, which is reduced to NO_2 and O^{2-} with the formation of the Li_2O passivation film[3], so the complete reaction can be rewritten as eqn 2. The corresponding capacities of the two voltage plateaux are 31.89 and 167.57 mAh g^{-1}, respectively, which equal to $Li_{0.78}$ WO_4 and $Li_{2.23}WO_4$ are obtained at the end of the two plateaux, respectively if all the WO_3 takes part in the reactions. However, the existence of unreacted WO_3 in the two discharged samples proves that the actual values are higher than 0.78 and 2.23. In addition, in view of the limited reaction efficiency, the theoretical values in these equations are also higher than 0.78 and 2.23 respectively.

$$WO_3 + xLi^+ + e^- \longrightarrow Li_xWO_4 \quad (1)$$

$$2WO_3 + 3NO_3^- + (2x + 2)Li^+ + (2x\text{-}1)e^- \longrightarrow 2Li_xWO_4 + 3NO_2 + Li_2O \quad (2)$$

For the discharged Li_2WO_4 samples, there is almost a one-to-one correlation between all the diffraction peaks and the JCPDS card of $7Li_2WO_4{\cdot}4H_2O$. As per the above-mentioned analysis, it is believed that Li_2WO_4 converts to $Li_{2+x}WO_4$ through a one-step lithium intercalation during discharge, as shown in eqn 3. It is calculated that the x value in $Li_{2+x}WO_4$ is 3.88 according to the actual discharge capacity of 397.09 mAh g^{-1}. The higher amount of lithium intercalated in Li_2WO_4 than WO_3 implies higher capacity of the Li_2WO_4 cathode.

$$Li_2WO_4 + xLi^+ + e^- \rightarrow Li_{2+x}WO_4 \quad (3)$$

Conclusion

The earlier cathode material for thermal batteries - WO_3 and its lithiated oxide Li_2WO_4 are re-evaluated and investigated as cathode materials for medium-temperature (200-300 °C) lithium batteries coupled with $LiNO_3$-KNO_3 and $LiNO_3$-KNO_3-$CsNO_3$ eutectics. The ternary electrolyte usually presents better electrochemical performance due to its lower melting point which brings better kinetics than binary electrolyte. Without frequent phase transitions which results to the increase of cell polarization, Li_2WO_4 presents much wider voltage plateaux and much higher capacities. It is believed that WO_3 and Li_2WO_4 both convert to lithium insertion $LixWO_4$ according to the XRD analysis. This preliminary study proves the better applicability of Li_2WO_4 in medium-temperature (200-300 °C) lithium batteries and more detailed studies are in progress.

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