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Screening Study of Mixed Transition-Metal Oxides for Use as Cathodes in Thermal Batteries

Ronald A. Guidotti and Frederick W. Reinhardt
Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185-0614

Abstract

Mixed transition-metal oxides were evaluated for possible use as cathodes in thermal batteries. Over 100 candidates were examined, including commercial materials and many that were synthesized in house. The mixed oxides were based on Ti, V, Nb, Cr, Mo, W, Mn, Fe, Co, Ni, and Cu doped with other transition metals. A number of individual (single-metal) oxides were included in the study for comparison. The candidates were tested in single cells with Li(Si) anodes and separators based on LiCl-KCl eutectic. Screening was done under constant-current conditions at current densities of 125 mA/cm^2 and, to a lesser extent, 50 mA/cm^2 at a temperature of 500°C. The relative performance of the oxide cathodes is discussed, along with the relative limitations of these materials.

Introduction

Potential future thermal-battery applications envision higher energy densities and lifetimes of up to four hours. The currently available technology will not meet these projected requirements, primarily due to limitations of the cathode material. The deficiencies in the currently available cathodes for use in thermal batteries has resulted in an effort at Sandia to develop new and improved cathode materials for these applications.

A number of characterization criteria must be examined when developing a new cathode material for thermal batteries. The ideal cathode would have the properties listed in Table 1. We have been evaluating both sulfide- and oxide-based transition-metal materials as potential cathodes. Some work with mixed Fe and Co sulfides has been reported by the Naval Surface Weapons Center *(1)*. However, the synthesis of such materials is somewhat complicated and the emfs are no better than that of FeS$_2$. We chose to focus initially on oxide systems, due to their ease of synthesis.

A number of workers have investigated various transition-metal oxides for thermal-battery cathodes. Researchers at the U.K. Defence Research Agency (DRA) spent considerable time investigating various lithiated vanadium-oxide (LVO) materials *(2-4)*. These materials were more thermally stable and had higher open-circuit voltages (OCVs) than FeS$_2$, but had lower capacities and exhibited sloping discharge curves due to intercalation reactions. There were also issues to resolve involving self-discharge. The DRA also studied oxides of Mn and Cr. While these materials had reasonably good open-circuit voltages (OCVs), they suffered in many cases from low electrical conductivity, capacities, and rates *(5)*. Work has been reported using lithiated oxides of V, Cr, Cu, Co, and Mo with mixed results *(6)*. Most of these materials showed intercalation reactions on discharge. The performance of a cathode based on V$_2$O$_5$ and carbon has been reported but it suffered from high self-discharge *(7)*.

Table 1. Attributes of An Ideal Cathode for Use in Thermal Batteries

- ♦ An emf of >3 V (vs. Li)
- ♦ Thermally stable to >800°C
- ♦ High electronic conductivity
- ♦ Good kinetics (high rate capability)
- ♦ Little or no solubility in molten salts
- ♦ Low equivalent weight (high coulombs/mole)
- ♦ Non-intercalating (multiphase) discharge
- ♦ Reaction products insoluble in molten salts, with high electronic conductivity and thermal stability
- ♦ Reasonable cost
- ♦ Environmentally friendly ("green")

In this paper, we report on single-cell screening studies with mixed transition-metal oxides evaluated for possible use as cathodes in thermal batteries. The mixed oxides were based on Ti, V, Nb, Cr, Mo, W, Mn, Fe, Co, Ni, and Cu doped with other transition metals. The relative performance and limitations of these materials are discussed.

Experimental

Cathode Preparation - The bulk of the oxides that were synthesized in house used the oxides directly or precursors based on carbonates, hydroxides, nitrates, and, in some cases, chlorides. In a typical preparation, a mixed oxide was prepared by first blending mixtures of carbonates of the constituent oxides. The mix was then heated in a platinum crucible in a furnace in a dry room (<3% relative humidity) at the appropriate temperature (typically between 700°C and 800°C) for four to twelve hours. A limited number of the more-refractory Co-Ti oxides were prepared by heating at a temperature as high as 1,350°C overnight.

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<u>Cells</u> - Single cells were 3.18 cm in diameter and were constructed using 44% Li/56% Si anodes and separators of LiCl-KCl eutectic containing 35% MgO.[1] The catholytes was prepared by blending 20-25% electrolyte or separator with the active cathode. For cathodes that were poor electronic conductors, 10-20% Lonza KS-15 graphite was added to the catholyte mix. For those mixes where there was a likelihood of carbon reduction of the oxide constituents, Mo powder was used as the conductive additive. After each test, the cell was post-mortemed and the separator examined for the presence of dissolved materials or reaction products.

<u>Test Procedure</u> - The cells were assembled in the dry room and were tested using temperature-controlled heated platens in a glovebox where the moisture and oxygen levels were each maintained at <1 ppm. The cells were tested under computer control at 500°C under constant-current conditions using a PAR 173A galvanostat. A background current density of 125 mA/cm^2 was applied for 55 s and a pulse current density of 250 mA/cm^2 was applied for 5 s during each 60-s cycle. Before application of the load, the cells were allowed to stand on open circuit for 30 s. In limited tests, cells were also tested at a fixed current density of 50 mA/cm^2.

Data from standard Li(Si)/LiCl-KCl-MgO/FeS_2 cells were used as a metric for comparison of relative performance of cells with the new cathodes. Cells were discharged until the cell voltage dropped to 1.25 V and the capacity to this point was then determined. A second metric was the polarization that occurred during the high-current 5-s pulses. From this data, an effective cell resistance could be calculated.

Results and Discussion

The results of the single-cell tests are summarized in Table 2 for all the oxides tested. (The data are normalized to the mass of active cathode. The voltage at 125 mA/cm^2 is the initial value upon placing the cell under load.) The materials are categorized by the parent or primary transition-metal oxide. Out of all the materials tested, only six materials had capacities of more than 1,000 coulombs/g and half of these were Ni based: Co_3O_4 (with Mo added), Ni_3O_4, NiO (black), NiO (green), V_2O_5 (with Mo added), and CuO. None of the oxides with OCVs of 3 V or more would sustain this voltage under load for very long, showing a rapid decline of potential with time.

Figures 1 and 2 show representative traces for a number of these oxides. Several materials that had exceptionally flat discharge traces also had lower-than-desired voltage under load. None of the W-based oxides could match the capacity and rate of FeS_2. Catholytes based on oxides of Mo were the poorest performing materials found in the study. They tended to show an initially high OCV that declined moderately or rapidly upon application of the load (see Fig. 1 for $CuVMoO_6$.) The capacities were generally greater than those for the corresponding W compounds and tended to decrease under a lighter load (50 mA/cm^2) due to increased self-discharge. The separator was darkened with the products of self-discharge reactions.

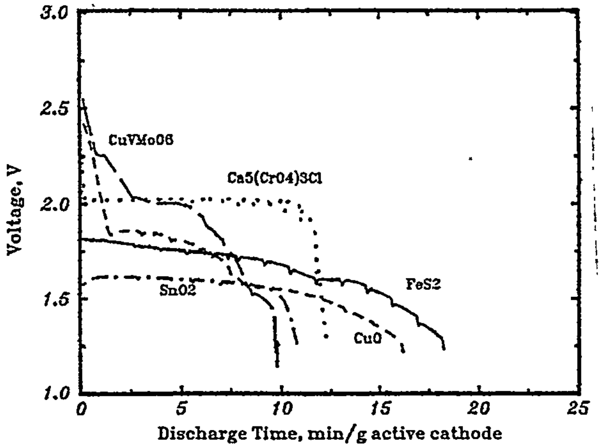

Figure 1. Discharge Traces for Some Oxides of Sn, Cu, Cr, and Mo at 125 mA/cm^2. Steady State/250 mA/cm^2 Pulse (55 s/5 s). The Discharge Trace for FeS_2 Is Included for Comparison.

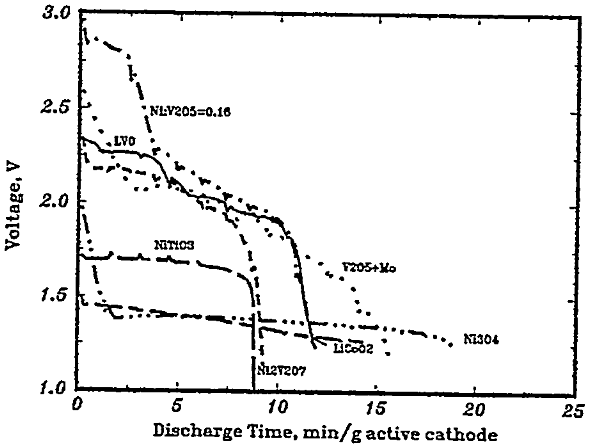

Figure 2. Discharge Traces for Some Oxides of Ni, Co, and V at 125 mA/cm^2. Steady State/250 mA/cm^2 Pulse (55 s/5 s).

Oxides of Ni and Co behaved similarly and tended to show an initial high voltage that quickly dropped to a flat, high-capacity plateau but with a voltage lower than FeS_2 (Fig. 1). Lithiated materials tended to have flat discharge profiles but at much lower voltages than reported for Li ambient-temperature cells. The voltage of $LiCoO_2$, for example, is ~4 V vs. Li at room tempera-

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[1] Unless noted otherwise, all compositions are reported as weight percent.

Table 2. Summary of Single-Cell Tests with Pure and Mixed Transition-Metal Oxides.[a]

Material	OCV @ 30 s, V	Volt. @ 125 mA/cm^2, V	Coul/g cath
FeS_2	1.92	1.34	1199
	W		
WO_2	2.17	1.17	7
$LiWO_3$	2.09	1.84	51
Li_2WO_4	N.A.	1.21	6
$CaWO_4$	N.A.	1.03	8
$CuWO_4$	1.69	1.26	15
$CoWO_4$	2.46	1.98	476
$MnWO_4$	N.A.	1.77	474
$NiWO_4$	2.53	2.04	480
$ZnWO_4$	N.A.	1.63	487
	Mo		
MoO3+Mo	2.60	1.68	152
MoO2	2.59	1.79	197
$CaMoO_4$	N.A.	1.82	107
$CuMoO_4$	1.88	1.62	73
Li_2MoO_4	2.36	1.58	290
$ZnMoO_4$	N.A.	2.10	453
$CuVMoO_6$	2.92	2.55	642
$CuV_{1.7}Mo_{0.3}O_6$	3.22	2.90	266
$CuV_{1.4}Mo_{0.6}O_6$	3.16	2.91	656
	Co		
Co_2O_3[b]	2.66	2.35	371
Co_2O_3	2.66	2.50	960
Co_3O_4+Ni	N.A.	2.06	1478
$NaCoO_2$	2.92	1.49	29
$LiCoO_2$[b]	2.32	1.33	12
$LiCoO_2$	2.29	1.50	954
	Ni		
Ni_3O_4	N.A.	1.97	1231
NiO (green)	2.19	1.62	1114
NiO (black)	2.15	1.84	1241
$LiNiO_2$	2.18	1.74	904
$LiMn_{0.3}Ni_{0.7}O_2$	2.49	1.66	61
$NaNiO_2$	2.14	1.73	175
$BaNiO_3$	2.41	2.17	110
$BaNi_2O_5$	2.16	1.83	62
$Ni_3(PO_3)_2$	2.40	2.05	636
	Mn		
MnO_2	3.24	3.09	324
Mn_3O_4	2.24	2.06	330
$LiMn_2O_4$+ Mo	N.A.	1.81	201
$LiCr_{0.4}Mn_{1.6}O_4$[b]	2.84	2.58	86
$Li_2Mn_4O_9$[b]	3.21	2.94	165
	Cr		
CrO_2	Thermal.	unstable	
$CoCrO_4$	2.52	1.83	441
$CoCr_2O_4$	2.20	1.78	454
$NiCr_2O_4$	2.37	2.10	672
$ZnCrO_4$+Ni	3.11	2.78	107
Ca_2CrO_4Cl	N.A.	2.07	412
$Ca_5(CrO_4)_5Cl$	N.A.	2.11	271
$Ca_5(CrO_4)_5Cl$[b]	N.A.	2.17	790
	V		
V_2O_5+Mo	2.81	2.59	1012
LVO[c]	N.A.	2.33	799
VO_2	3.08	2.89	577
VO_2[b]	N.A.	2.76	825
$LiVO_3$	2.82	2.66	574
Li_3VO_4[b]	3.42	3.20	322
$LiMnVO_{3.5}$	3.06	2.58	297
$LiMn_{1.5}V_{0.5}O_{3.75}$[n]	3.11	2.72	67
$LiMn_{1.75}V_{0.25}O_{3.875}$[b]	3.11	2.76	54
$9V_2O_5.MoO_3$[b]	3.48	3.26	828
$V_2O_5.MoO_3$[b]	3.42	3.16	639
$9V_2O_5.WO_3$[b]	3.49	3.31	696
CaV_2O_6	2.92	2.75	387
CoV_2O_6[b]	3.05	2.47	351
CuV_2O_6	2.92	2.51	505
FeV_2O_6[b]	3.29	3.01	650
$CrVO_4$[b]	3.07	2.30	196
NiV_2O_6[b]	3.36	3.04	684
$Co_2V_2O_7$[b]	3.07	2.65	340
$Fe_2V_2O_7$[b]	3.17	2.87	582
$Ni_2V_2O_7$	3.08	2.81	545
$Co_3V_2O_8$[b]	2.99	2.09	208
$Fe_3V_2O_8$[b]	3.21	2.92	614
$Ni_3V_2O_8$	2.49	2.08	406
$Ni_3V_2O_8$[b]	3.39	3.06	763
$NiO:V_2O_5=0.16$	3.38	2.97	766
LiV_3O_8	3.13	2.89	719
KV_5O_{13}[b]	3.34	3.10	421
$K_5V_8O_{21}$[b]	3.34	3.10	432
$K_{0.27}V_2O_5$[b]	3.30	3.07	634
$LiCuVO_4$[b]	2.88	2.61	86
$LiNiVO_4$	2.75	2.23	307
$LiNiVO_4$[b]	3.04	2.26	379
$VOSO_4$	3.10	2.78	613
	Ti		
$CoTiO_3$	2.09	1.87	670
$CuTiO_3$	2.55	2.38	741
$FeTiO_3$[b]	2.96	2.06	415
$MnTiO_3$	N.A.	1.01	6
$NiTiO_3$	2.22	1.71	576
Co_2TiO_4[b]	2.43	1.31	469
$CoTi_2O_5$[b]	2.49	1.48	345
	Misc		
$LiFe_5O_8$	2.39	1.81	291
$CuFe_2O_4$	2.45	2.23	433
CuO[b]	N.A.	2.00	1847
Nb_2O_5	N.A.	2.03	484
NbO_2	1.98	0.99	7
$LiTa_2O_6$	1.98	1.14	7
PbO_2	2.37	2.04	400
$Pb(III,IV)O_x$	2.32	1.94	537
$BaPbO_3$[b]	2.35	1.26	12
SnO_2	N.A.	1.57	692

[a] Unless noted otherwise, all catholytes contained graphite as the conductive additive. Voltage is that upon application of the load. Data are normalized to active mass of cathode material.

[b] No conductive additive.

ture *(9)*. At 500°C, however, the potential is only 1.5 V (Fig. 2) because of a change in the discharge mechanism. Cathodes with this high a potential would oxidize the chloride to the LiCl-KCl eutectic to chlorine gas which would result in an sustained cell emf of ~3.5 V at this temperature. We saw no evidence of this during discharge of our cells.

Undoped MnO_2 becomes thermally unstable at 500°C but the lower oxides are stable. Like $LiCoO_2$, MnO_2 is also a high-voltage cathode (~4 V vs. Li) that has been used in Li ambient cells where it exhibits intercalation behavior. The lithiated and doped oxides of Mn showed high, initial OCVs with short, sloped discharges typical of intercalation

The chromites that were tested showed erratic behavior and had high resistances. The voltages for cells with chromates dropped rapidly under load. Only the Cr(V) material, $Ca_5(CrO_4)_3Cl$ (Fig. 1), showed any promise. It had a potential over 2 V under load but had a lower capacity than FeS_2 and a higher resistance. The area under the discharge curve is proportional to the gravimetric energy density. In this regard, $Ca_5(CrO_4)_3Cl$ was identical to FeS_2.

Oxides based on V were the most extensively examined in this work. Doping with Ni gave the highest voltage but these plateaus were usually very short. The oxide with a $Ni:V_2O_5$ mole ratio of 0.16 gave one of the highest voltages (Fig. 2) but the voltage quickly dropped to that of the undoped or lithiated materials during discharge (Fig. 2). The discharge processes tended to be more complicated with the doped V_2O_5 because of the large number of possible oxidation states for V (II, III, IV, and V) and the dopant (II and III). The general tendency was, not unexpectedly, for intercalation reactions to predominate. The doped V oxides tended to show higher capacities at the lower rate (50 mA/cm^2), except for the Cu-doped materials.

The titanates performed better than expected and exhibited very flat discharges but, unfortunately, only at potentials <2 V, as seen for $NiTiO_3$ in Figure 2. Nb_2O_5 performed better than NbO_2 but showed a declining voltage with discharge. Ta_2O_5 could not sustain discharge at all. Pb oxides, lithiated Fe_2O_3, and Cu-substituted Fe_2O_3 performed poorly as cathodes when discharged at 125 mA/cm^2.

Pure CuO had a high capacity (Fig. 1) but showed multiple lower-voltage plateaus due to the different phases that formed during discharge. This was also noted by Ritchie *(8)*. Cu-doped oxides suffered from migration and solubility problems that resulted in reduction of Cu(II) at the anode. (Ritchie avoided this problem by using a solid electrolyte.) These materials tended to exhibit extensive formation of Cu that could easily short cells with thin separators.

Conclusions

We screened a large number of mixed transition-metal oxides and some undoped oxides as possible cathodes for use in thermal batteries. The oxides were based on Ti, V, Nb, Cr, Mo, W, Mn, Fe, Co, Ni, and Cu and were doped with various transition metals. The doped and undoped oxides were tested in single cells at 500°C at 125 mA/cm^2 steady state (55 s) with 250 mA/cm^2 pulses (5 s). Except for MnO_2 and CrO_2, all the materials tested have higher thermal stabilities than FeS_2. Materials with greater emfs then FeS_2 had lower gravimetric coulombic capacities. Those with greater or comparable capacities–Co_3O_4, Ni_3O_4, NiO (black and green), V_2O_5, and CuO–have either a high initial voltage that quickly drops to a lower-voltage plateau, or gradually declines during discharge due to intercalation reactions. Cu-doped oxides show unacceptable self-discharge and extensive formation of Cu dendrites into the separator.

Some materials that are too resistive for the standard discharge conditions show acceptable performance when tested under light-load conditions (50 mA/cm^2). These include: $NiWO_3$, $CoTiO_3$, Co_2O_3, $LiFe_5O_8$, and Ni-doped V_2O_5 (e.g., NiV_2O_6, $Ni_2V_2O_7$). The latter materials deserve further attention.

The Cr(V) compound, $Ca_5(CrO_4)_3Cl$, has a higher emf than FeS_2, a lower gravimetric capacity (C/g), a higher resistance, and a similar energy density. The volumetric capacities (C/cc) for the two catholytes are very similar which makes this material promising for select applications.

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