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SOLUTE AND CATHODE INVESTIGATIONS IN PROPYLENE GLYCOL SULFITE

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SUMMARY

A screening investigation was conducted to determine the potentialities of propylene glycol sulfite as an electrolyte solvent for high-energy-density batteries. The first series of tests was made to determine which solute produced the most highly conducting electrolyte solution with the aforementioned solvent. Morpholinium hexafluorophosphate, lithium perchlorate, and potassium hexafluorophosphate were the best solutes. A second series of tests was made to find the best cathode for use in a cell with a lithium anode. Cupric nitrate was the best cathode tested, with an open-circuit voltage of 3.85 volts and a current density of 7.1 milliamperes per square centimeter at a cell voltage of 3.00 volts. Tests were next made with a modified Wheatstone bridge. These tests indicated that the impedances of the cells were very high (100 to 300 ohms). Compatibility tests on the more promising systems, such as lithium/lithium perchlorate in propylene glycol sulfite/cupric nitrate trihydrate indicate a shelf life of less than 2 days, while in the same system with lead dioxide substituted for the cupric nitrate trihydrate, the life was more than 2 weeks. However, the more stable systems were composed of heavy metal oxides, such as lead dioxide and vanadium pentoxide, which did not produce so high a voltage or current density as the lighter metal compounds for the test period. These more stable systems would, therefore, yield a lower-energy-density battery.

INTRODUCTION

The development of a high-energy-density battery is basically dependent upon achieving mutual compatibility of an electrochemically suitable electrolyte with highly reactive anode and cathode materials. Because of the high-theoretical-performance potentialities of anode-cathode couples with lithium as the anode material, substantial effort has been devoted to searching for electrolytes and cathode materials that most favorably accommodate the lithium anode.

As part of the study of advanced battery concepts being conducted by the Lewis Research Center, an organic electrolyte solvent screening program was conducted with emphasis on the sulfur derivatives. The results of this investigation indicate that the most promising solvent was propylene glycol sulfite with respect to compatibility with lithium and its ability to produce solutions with lithium perchlorate having good conductivity (ref. 1).

The program was then extended to determine the best conducting solute in propylene glycol sulfite and to evaluate several cathodes in cells with a lithium anode. A total of 26 solutes were selected for evaluation based on established abilities to produce high-conductivity solutions in water and organic solvents in general. The cathode evaluations were short-term qualitative tests to single out the most promising materials for later long-duration compatibility studies. The most promising combinations, selected on the basis of voltage output and operating time under load and apparent reversibility, were evaluated for compatibility. This evaluation was accomplished by testing the anodes and cathodes separately with the electrolyte and also as complete anode-cathode-electrolyte combinations.

APPARATUS AND PROCEDURE

The solute evaluations utilized a tubular glass cell, 1/2 inch (1.3 cm) in diameter by 3 inches (7.6 cm) long with a pair of platinum electrodes (cleaned in aqua regia) having an area of 1.28 square centimeters on each face. The conductance was first determined at constant temperature with propylene glycol sulfite only in the cell. This determination was accomplished by removing the solvent from its bottle with a hypodermic syringe and placing it in the tubular cell. The solute to be investigated was then added to the solvent until the solution was saturated and excess solid solute was present in the bottom of the tube. The solution was then brought to constant temperature in a water bath, and the conductivity was measured again. The measurements were made with a modified Wheatstone bridge operating at a frequency of 1000 cps (1000 Hz). Finally, any visual change in the electrolyte was noted.

The individual cell screening tests were prepared in the following manner: The cathode was prepared by grinding the compound to be tested with activated carbon (50 percent by volume of each to increase conductivity) in a mortar. During the grinding a small amount of the electrolyte to be used in the cell test was added to act as a binder. The mixture was placed in a mold on top of a piece of nickel wire screen (1.28-sq-cm area, 20 mesh, 0.016-in. (0.04-cm) wire diameter) and compacted to a pressure of 3000 psi. The composite was then dried for 24 hours in air at room temperature. The lithium anode was cleaned by filing a piece of the metal to expose a bright surface. The electrodes were spaced by using cardboard spacers 0.030 inch (0.076 cm) thick. The electrode assembly was then clamped together with a C-clamp and lowered into a beaker of electrolyte (propylene glycol sulfite saturated with lithium perchlorate), and the cells were discharged through an external constant resistance. The voltage under load was recorded continuously, along with periodic open-circuit readings. The test was concluded when the cell voltage fell 0.2 volt from its stable load value. The open-circuit voltage was again measured to see whether the voltage would return to the original value. The impedance of the system was determined by use of a modified Wheatstone bridge. The current was calculated from Ohm's law.

The following procedure was used in determining the compatibility of the various cell components: A test tube was cleaned and solvent added. Then enough solute was added to saturate the solution and leave excess solute on the bottom. The cathode compound was added to the tube as a powder which also settled to the bottom. A piece of clean lithium metal was added to serve as the anode. This lithium floated on the surface. The distance between anode and cathode materials was about 1 inch (2.5 cm). Observations were made daily for gross chemical changes, which in all cases were easily seen, as a means of determining chemical stability.

RESULTS AND DISCUSSION

Preliminary screening results discussed in reference 1 indicate that propylene glycol sulfite has good conductivity when saturated with lithium perchlorate (3.3×10^{-3} $\text{ohm}^{-1}\text{cm}^{-1}$) and stability with lithium to warrant more detailed evaluation. Consequently, a total of 26 solutes as well as several cathode materials were selected for evaluation to define (within the limits of the selections) the best combination for use with a lithium anode.

The conductivities of a large number of salts in propylene glycol sulfite are given in table I. The conductivity of the solvent was determined in order to confirm its purity. There was a slight variance in the conductance of the solvent which could not be explained (table I, column 3). The best solute evaluated was morpholinium hexafluorophosphate with a conductivity of 3.6×10^{-3} ohm^{-1} centimeter^{-1}. Lithium perchlorate was second best with a conductivity of 3.3×10^{-3} ohm^{-1} centimeter^{-1}; potassium thiocyanate showed promise on a conductivity basis, but decomposition took place with the formation of a yellow precipitate.

The conductivity of some salts to be used as cathodes was measured in order to detect solubility not apparent by visual inspection on adding the salt to solvent. The best performing cathodes, cupric chloride and cupric nitrate, dissolved in the solvent and produced an increase in conductivity (table I), while all other cathodes tested showed no increase in conductivity.

The results of the cell screening tests which were performed are given in table II. Tests 2 and 3 were made to determine how the conductive portion of the cathode behaved in the absence of active material. Test 2 used an anode of lithium metal ribbon containing twice the amount of lithium needed for the cathode. The electrolyte was propylene glycol sulfite saturated with lithium perchlorate. The cathode contained only activated carbon on the nickel screen. Test 3 with the same anode and electrolyte as in test 2 used only a nickel screen cathode. The voltage of test 3 was the lowest in the table. The fact that cell 2 delivered current to a load was attributed to the presence of adsorbed oxygen on the activated carbon. Dashed lines in the table indicate that data were not taken.

The most promising cathodes based on open-circuit voltage and discharge performance with a 427-ohm load were cupric nitrate, cupric sulfate, and cupric chloride, with values decreasing in that order. Vanadium pentoxide and lead dioxide looked promising on the basis of these criteria; however, the weight of these compounds is high. The various cathodes are discussed further in connection with the compatibility tests. The 427-ohm load resistance used in all the tests was selected during test 1, since its use resulted in cell operation at or near 2.00 volts. The duration of each test was determined by the shape of the voltage curve. (A flat curve is desirable.) When the stable load voltage decreased 0.2 volt or more, the test was discontinued because in the screening of systems, it was felt that current drain and voltage level were the most important initial items. Those systems which looked promising could be rechecked at a later date for capacity. An open-circuit voltage reading taken at the end of each test was used to evaluate the capability to return to original open-circuit voltage. The current density shown in table II was calculated from the voltage, the load resistance, and the cathode area. Measurements made with a modified Wheatstone bridge indicate high impedance in the cells.

The results of the compatibility tests are shown in table III. All the materials tested were selected on the basis of performance in the cell tests shown in table II. These materials were selected either for having high open-circuit or load voltage or for displaying a very flat discharge curve at more moderate voltages near 2.00 volts.

The only cathode which showed no signs of reacting in a cell for 2 weeks was lead dioxide. The promising systems such as lithium/lithium perchlorate in propylene glycol sulfite/cupric chloride dihydrate or cupric nitrate trihydrate reacted in less than 24 hours, as indicated by a color change. The presence of water of hydration contained in the cathode salts probably aided in the speed of the reaction. However, further work in the purification of cell components would be needed to verify this conclusion.

CONCLUSIONS

In an investigation to determine the best solute for maximum electrochemical conductivity with propylene glycol sulfite as the solvent, the following conclusions were drawn:

1. Of the solutes investigated, the best solute in propylene glycol sulfite was morpholinium hexafluorophosphate with a conductivity of 3.6×10^{-3} ohm^{-1} centimeter^{-1}. Lithium perchlorate was next with a conductivity of 3.3×10^{-3} ohm^{-1} centimeter^{-1}.
2. The highest voltage levels and current drain rates were obtained with cupric nitrate, cupric sulfate, and cupric chloride, with values decreasing in that order.
3. Compatibility tests indicate that the best performing high-energy-density cells such as lithium/lithium perchlorate in propylene glycol sulfite/cupric nitrate trihydrate would have a shelf life of not more than 24 hours. Removing the water of hydration from the cathode would be a logical step to evaluate improvement in shelf life.
4. An unhydrated metal oxide, such as lead dioxide, was compatible with lithium and the electrolyte for at least 2 weeks, which was the duration of the tests.
5. Wheatstone bridge measurements indicate that the impedances of all the cells tested were high.

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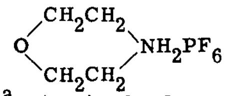
120-34-01-09-22.

REFERENCES

1. Abens, Sanders G.; Mahy, Tyler X.; Merz, William; and Meyers, William F.: Development of High Energy Density Primary Batteries 200 Watt Hours Per Pound Total Battery Weight Minimum. Final Rep., Livingston Electronic Corp. (NASA CR-54803), 1965.
2. Meyers, William F.: Development of High Energy Density Primary Batteries 200 Watt Hours Per Pound Total Battery Weight Minimum. Final Rep., Livingston Electronic Corp. (NASA CR-54083), 1963.
3. Weast, Robert C., ed.: Handbook of Chemistry and Physics. 45th ed., Chemical Rubber Co., 1964.
4. Johnson, Richard E.: Electrolyte Solvent Properties of Organic Sulfur Derivatives. NASA TM X-1283, 1966.

TABLE I. - CONDUCTIVITY OF SOLUTES IN PROPYLENE GLYCOL SULFITE

Salt		Temperature, °C	Conductivity, $ohm^{-1}\ cm^{-1}$, of -		Appearance
Name	Formula		Solvent	Saturated solution	
Lithium sulfate trihydrate	$LiSO_4 \cdot 3H_2O$	25	6.1×10^{-6}	6.1×10^{-6}	--------------
Potassium iodide	KI	25	6.1	1.1×10^{-4}	Yellow solution
Lithium perchlorate	$LiClO_4$	25	6.0	3.3×10^{-3}	--------------
Potassium hexafluoride	KPF_6	25	6.0	1.5	--------------
Lithium fluoride	LiF	25	5.9	5.9×10^{-6}	
Lithium nitrate	$LiNO_3$	25	6.4	7.3×10^{-5}	--------------
Lithium iodide	LiI	25	5.8	5.3×10^{-4}	Yellow solution
Lithium bromide	LiBr	25	6.6	7.4	--------------
Lithium chloride	LiCl	25	7.0	4.1×10^{-5}	--------------
Cupric chloride dihydrate	[a]$CuCl_2 \cdot 2H_2O$	25	6.9	5.1	--------------
Manganese dioxide	[a]MnO_2	25	5.8	5.8×10^{-6}	--------------
Lead dioxide	[a]PbO_2	25	5.8	5.8	--------------
Cupric oxide	[a]CuO	25	5.8	5.8	--------------
Nickel oxide	[a]NiO	25	5.8	5.8	--------------
Vanadium pentoxide	[a]V_2O_5	25	5.8	5.8	--------------
Silver chloride	[a]AgCl	25	5.8	5.8	--------------
Ammonium dichromate	$(NH_4)_2Cr_2O_7$	25	5.4	5.4	--------------
Potassium iodate	KIO_4	25	5.4	8.5	--------------
Sodium acetate	$NaC_2H_3O_2$	25	5.2	9.5	--------------
Ammonium iodide	NH_4I	25	5.3	3.0×10^{-4}	Yellow solution
Potassium ethyl xanthate	CH_3CH_2OCSSK	20	5.5	4.7	Yellow, cloudy solution
Potassium fluoroborate	KBF_4	25	1.3×10^{-5}	2.9×10^{-5}	--------------
Potassium thiocyanate	KSCN	25	1.9	1.4×10^{-3}	Yellow precipitate
Morpholinium hexafluorophosphate	 $O(CH_2CH_2)_2NH_2PF_6$	25	2.3	3.6	--------------
Cupric nitrate trihydrate	[a]$Cu(NO_3)_2 \cdot 3H_2O$	25	1.5	1.0×10^{-4}	--------------
Lithium glycolate	$HOCH_2COOLi$	25	2.3	5.1×10^{-5}	--------------

[a] Cathode.

TABLE II. - EXPERIMENTAL CELL TESTS

[Lithium anode/saturated lithiun perchlorate in propylene glycol sulfite/test cathode.]

Test	Cathode		Open-circuit voltage, V	Cell voltage under 427-ohm load resistance, V	Time of final open-circuit voltage reading, min	Open-circuit voltage at end of test, V	Current under load, mA (a)	Cell impedance,[b] ohms	Calculated cell resistance, ohms
	Name	Formula							
1	Manganese dioxide	MnO_2	3.35	1.95	60	2.70	4.6	80.0	304
2	Carbon nickel	C/Ni	3.15	1.90	25	2.70	4.4	----	282
3	Nickel	Ni	2.95	.20	15	2.75	.2	----	13 750
4	Cupric chloride dihydrate	$CuCl_2 \cdot 2H_2O$	3.45	2.70	20	3.30	6.5	----	115
5	Silver chloride	AgCl	3.30	2.25	40	2.80	5.3	54.1	185
6	Cupric bromide	CuBr	3.10	2.37	45	2.70	5.6	40.0	130
7	Nickel chloride hexahydrate	$NiCl_2 \cdot 6H_2O$	3.27	2.00	60	2.70	4.7	64.0	270
8	Chromium trichloride hexahydrate	$CrCl_3 \cdot 6H_2O$	3.25	2.10	80	2.65	4.9	70.0	233
9	Cupric nitrate trihydrate	$Cu(NO_3)_2 \cdot 3H_2O$	3.85	3.00	45	3.85	7.1	95.0	120
10	Vanadium pentoxide	V_2O_5	3.50	2.65	23	3.15	6.2	62.0	137
11	Cupric oxide	CuO	3.30	2.07	12	2.80	4.8	----	250
12	Nickel oxide	NiO	3.30	2.40	5	2.60+	5.6	----	160
				2.00	30		4.7	----	280
13	Lead dioxide	PbO_2	3.87	2.55	30	3.30	6.0	----	220
14	Cobalt trichloride hexahydrate	$CoCl_3 \cdot 6H_2O$	3.40	1.95	12	2.80	4.6	----	320
15	Cupric sulfate trihydrate	$CuSO_4 \cdot 3H_2O$	3.60	2.70	40	3.45	6.5	----	150
16	Silver iodide	AgI	3.20	1.90	45	2.60	4.4	----	293

[a] Area of electrode, 1 sq cm.

[b] Frequency of bridge, 1000 cps (1000 Hz).

TABLE III. - COMPATIBILITY TESTS

[Solvent, propylene glycol sulfite.]

Test	Solute		Cathode		Anode		Time	Observation	Comments
	Name	Formula	Name	Formula	Name	Formula			
1	---------------------------	-------	-----------------------	--------------	Lithium	Li	3 weeks	No change	Stable
2	Ammonium iodide	NH_4I	-----------------------	--------------	Lithium	Li	5 days	Precipitate on anode	---------------
3	Lithium perchlorate	$LiClO_4$	-----------------------	--------------	Lithium	Li	3 days	Excess salt disappeared	Salt reacted with solvent
4	Potassium hexafluorophosphate	KPF_6	-----------------------	--------------	Lithium	Li	3 days	Excess salt disappeared	Salt reacted with solvent
5	---------------------------	-------	Cupric nitrate trihydrate	$Cu(NO_3)_2 \cdot 3H_2O$	-------	--	1 week	Salt color changed to white	---------------
6	Lithium perchlorate	$LiClO_4$	Cupric nitrate trihydrate	$Cu(NO_3)_2 \cdot 3H_2O$	-------	--	3 weeks	Rapid gas evolution	Unstable
7	Lithium perchlorate	$LiClO_4$	Cupric nitrate trihydrate	$Cu(NO_3)_2 \cdot 3H_2O$	Lithium	Li	3 hr	Rapid gas evolution	Unstable
8	Potassium hexafluorophosphate	KPF_6	Cupric nitrate trihydrate	$Cu(NO_3)_2 \cdot 3H_2O$	Lithium	Li	5 days	Blue salt turned white	---------------
9	Potassium hexafluorophosphate	KPF_6	Cupric chloride dihydrate	$CuCl_2 \cdot 2H_2O$	Lithium	Li	1 day	Salt edges changed to yellow and then green	Unstable
10	Potassium hexafluorophosphate	KPF_6	Lead dioxide	PbO_2	Lithium	Li	1 day	No change	Stable

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