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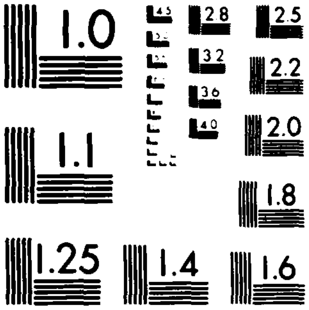

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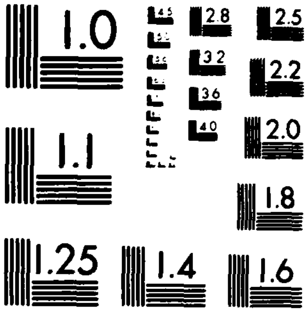

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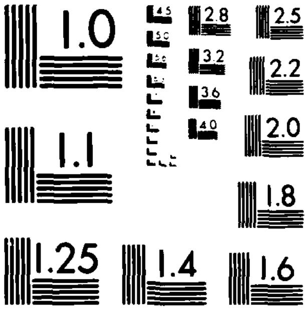

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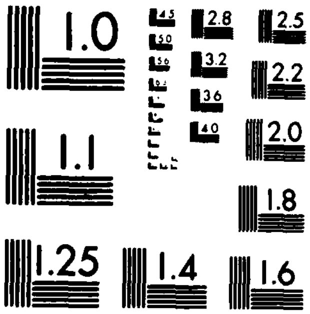

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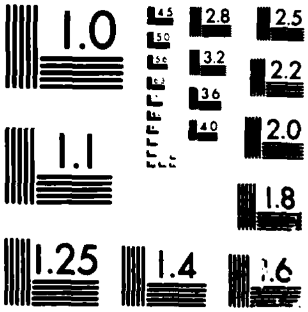

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A NEW BONDED CATALYST FOR SAFE LITHIUM-THIONYL CHLORIDE BATTERIES

Final Technical Report

F. Walsh and J. Hopewood
August 1982

to

U. S. Army Electronics Research and
Development Command
Fort Monmouth, NJ

Prepared by

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228 Main Street
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Buzzards Bay, MA 02532

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The goal of the research effort was to demonstrate that a new class of organometallic cathode catalysts, the TAAs, are stable in thionyl chloride and that they significantly improve the power performance of lithium-thionyl chloride primary batteries

A number of TAAs were evaluated and shown to be active catalysts. Included in this evaluation were TAAs which were

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~~20.~~) covalently bonded to the supporting carbon electrode material; a covalently bonded catalyst has the potential advantage that it will not dissolve into the electrolyte and negatively affect anode performance.

During the six month research program, the TAAs were shown to:

1. significantly improve cathode performance in $Li/SOCl_2$ cells;
2. improve cathode capacity;
3. improve cathode performance throughout long-term tests; and
4. not affect anode performance.

Further work is needed to develop data in cell studies on temperature range, shelf life, voltage delay effects, energy/power density as a function of rate, and factors affecting electrode capacity. Battery performance in stress tests to develop safety and cost data is also needed. ←

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This report discloses an invention. Distribution is limited to U. S. Government personnel pending patent review.

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1.0 Summary

The goal of the Phase I research effort was to demonstrate that a new class of organometallic cathode catalysts, the TAAs, are chemically stable in thionyl chloride and that they significantly improve the power performance of lithium-thionyl chloride primary batteries. These goals were met and exceeded. The TAAs, acting as cathode catalysts, provided cells with significantly improved voltaic performance and electrode capacity. This performance improvement remained throughout a long-term study. Lithium-thionyl chloride batteries, using TAA catalysts, will have the highest available energy and power densities for a primary battery system and a good expectation of safe and reliable long-term use.

A number of TAAs were evaluated and shown to be active catalysts. Included in this evaluation were TAAs which were covalently bonded to the supporting carbon electrode material; a covalently bonded catalyst has the potential advantage that it will not dissolve into the electrolyte and negatively affect anode performance.

During Phase I, the TAAs were shown to:

1. significantly improve cathode performance in $Li/SOCl_2$ cells;
2. improve cathode capacity;
3. improve cathode performance throughout long-term tests; and
4. not affect anode performance.

Further work is needed to develop data in cell studies on temperature range, shelf life, voltage delay effects, energy/power density as a function of rate, and factors affecting electrode capacity. Battery performance in stress tests to develop safety and cost data is also needed.

1.1 Program Objective

The objective of the Phase I research effort was to determine the chemical stability and the electrochemical activity of the TAAs in thionyl chloride. Demonstration that the TAAs are stable and electrochemically active means that they can be routinely used to significantly improve the energy and power densities of what is now a high energy/power density primary battery system ($Li/SOCl_2$) and at the same time improve the safety and reliability of this battery type.

1.2 Technical Approach

The Phase I research program was by necessity (due to its short duration and low funding level) only an initial evaluation program. Tests were carried out which provided the maximum amount of information with a minimum amount of expense or effort. In-house technologies in electrode fabrication and in cell testing derived from on-going primary fuel cell research were relied on, even though they did not necessarily provide an optimum picture of the performance characteristics of the TAAs. No effort was made to optimize the cathode or the cell system structures; optimization of electrolyte components was also not attempted. Reference data for cathode performance comparison purposes were either generated under the program or taken from a small sampling of the literature.

All the experimental data obtained were based on at least two separate but identical tests to ensure reliable data. The experimental procedures carried out included synthesis of various metallated TAAs, preparation of catalyzed carbons, fabrication of cathodes from catalyzed and uncatalyzed carbons, electrochemical evaluation (performance and capacity) of the cathodes, and long-term stress-test cathode evaluation. Test apparatus and procedures used are summarized in Section 2.

1.3 Reported Cathode Performance

A cathode now used commercially in $Li/SOCl_2$ batteries is comprised of a porous matrix of high surface area carbon black (Shawinigan Acetylene Black 50% C) and Teflon^R (approximately 5% by weight)[1]. Such batteries are designed for low rate discharge applications ($I < 10$ mA/cm^2); high rate discharge batteries are generally not used due to the poor performance of the cathode and the resulting safety hazards. Improving the performance of high-rate discharge $Li/SOCl_2$ batteries would be advantageous from a safety standpoint because it would allow this system to replace the hazardous Li/SO_2 system now used.

The safety hazard of $Li/SOCl_2$ batteries has been explored by several investigators[2-4]. The explosions observed were reported to result from oxidation of unstable cathodic reaction species at the anode which results in rapid heat evolution in excess of that due to cell overvoltage or cell current. A cathode with improved electrochemical performance would have lower overvoltage and more complete reduction of $SOCl_2$, thus allowing for sustained high-rate discharge at a comparably lower rate of heat generation and of unstable reaction by-product generation.

Dey[5] evaluated the performance of various carbons as cathodes in $Li/SOCl_2$ cells. The best carbon used in his experiments was Shawinigan Acetylene Black which, when fabricated into a D-cell, had a maximum electrode capacity of approximately 3 A-hr/g-carbon for a discharge of 30 mA (0.2 mA/cm^2). At high discharge rates (3 A; 18 mA/cm^2), other carbons (ie.: Vulcan XC-72R) were found to be as good, although the electrode capacity for all carbons tested was significantly lower (ie.: 1.2 A-hr/g-carbon).

Doddapaneni[6,7] evaluated the use of iron or cobalt phthalocyanine as a cathode catalyst in $Li/SOCl_2$ cells. The iron phthalocyanine (FePc) improved performance, but it rapidly leached out of the cathode and was used as a solution of 1 to 3 mg catalyst/ml of electrolyte. Polymeric cobalt phthalocyanine-catalyzed (CoPc) cathodes contained 5% catalyst by weight. Average cell voltage (50% discharge) improvements for FePc and CoPc over Shawinigan Acetylene Black (100% SAB) were reported at 40 and 230 mV on 3.03 V at 20 mA/cm^2, respectively[7]. Cathode capacity at 20 mA/cm^2 was reported as 0.65, 0.75 and 1.2 A-h/g for Shawinigan Acetylene Black, CoPc and FePc respectively[7]. CoPc, incorporated into the cathode, only improved the performance of the carbon slightly; FePc improved the performance significantly, but no data were provided on the performance of the anode over time in the presence of FePc in the electrolyte. The cathode capacity results of Doddapaneni for FePc[7], while significantly improved over his carbon control, do not show its actual performance to be improved over the performance of neat carbon reported by Dey[5] (ie.: both at 1.2 A-h/g-carbon).

1.4 New Catalysts

Cathode catalysts for lithium-thionyl chloride batteries will improve voltaic performance and thereby improve power and energy densities. Reduced overvoltages and decreased production of unstable cathodic reaction products resultant from cathode catalysts will improve battery safety. The organometallic catalysts previously used provide cathodes with improved performance, but these catalysts dissolve into the electrolyte reducing both cathode and anode performance. The ECO catalysts tested under Phase I, provide cathodes with superior performance and increased capacity; long-term stability was observed. The general synthetic protocols used in preparing the catalyzed carbons is provided in Section 3; the performance of catalyzed cathodes is provided in Section 4. A list of catalysts tested along with their identifying codes is provided in Appendix A.

2.0 Experimental Procedure and Apparatus

2.1 Electrodes

The anode used was supplied by Battery Engineering, Inc. (Hyde Park, MA) and consisted of a thin (less than 50 mm) piece of lithium metal pressed into a 1 cm^2 square nickel EX-MET screen; the wire nickel current collector was spot welded to the screen. Anodes were stored in a dessicator under vacuum and transferred in a dry box to the cell.

The reference electrode consisted of a lithium ribbon wrapped around a nickel wire and held in a glass Luggin capillary tube. This tube was inserted into the electrolyte and held near the cathode during cathode evaluation.

Cathodes were prepared by mixing the carbon (catalyzed or uncatalyzed) with an aqueous dispersion of PTFE (ICI AD1) to achieve a fixed (generally 19:1) weight ratio. The mixture was diluted with deionized water and the solution mixed for 10 minutes using an ultrasonic bath. The solids were flocced using 10^{-2} M $CaSO_4$ and pH adjustment, and then rapidly filtered into a thin (0.2 mm) carbon support (Stackpole Fiber Co.). Excess water was removed with blotting paper, and a nickel screen (EX-MET) was pressed into the face of the electrode. Finally, the electrode was dried at 100°C for two hours to drive off the surfactant (Triton X-100) in the PTFE and then heat-treated at 300°C under a nitrogen atmosphere for five minutes to sinter the PTFE. The final cathode thickness (excluding the metal screen) was approximately 0.20 mm (0.01 in.) and carbon/catalyst loading was 15 mg/cm^2. The electrodes were prepared as 5 cm^2 disks from which 0.5 cm^2 disks were cut for testing in the cell.

2.2 ECO Test Cell

The test cell consisted of a glass cell body, a plastic cap and a plastic outer jacket, positioned in a Hydrovoid glove box under an atmosphere of dry air (Figure 1). The cathode was secured and positioned parallel to, but one centimeter from, the cathode. The tip of the Luggin capillary was positioned flush against the cathode. The cell electrolyte volume was 50 ml; the electrolyte was dry ($<$ 100 ppm water) 1.8 M $LiAlCl_4$ in $SOCl_2$ supplied by Battery Engineering Inc. The anode material, the electrolyte, the current collectors, and the Shawinigan Acetylene Black were thus all materials used commercially in $Li/SOCl_2$ batteries.

The cell and electrodes were assembled and tested in a Hydrovoid glove box under a positive pressure of dry air ($<$ 1 ppm water). Electronic connections to the potentiostat were made using a multiconductor cable which was inserted through the glove box wall.

2.3 Polarization Data

Cathode polarization data were obtained using an ECO Model 552 potentiostat; all data obtained were IR free. The area of the cathode (0.5 cm^2) was chosen due to the electronic constraints of this potentiostat: the IR-feedback system of this instrument could not compensate for the ohmic drop across the electrolyte at currents over 200 mA.

Polarization data were taken over a ten minute period by increasing slowly the current density up to 100 mA/cm^2 and recording the observed cathode potential vs the reference electrode.

2.4 Cathode Capacity Data

Cathode capacity data were obtained using the ECO Model 552 potentiostat to maintain a constant load (20 mA/cm^2). Polarization data (cathode vs reference) were recorded at five minute

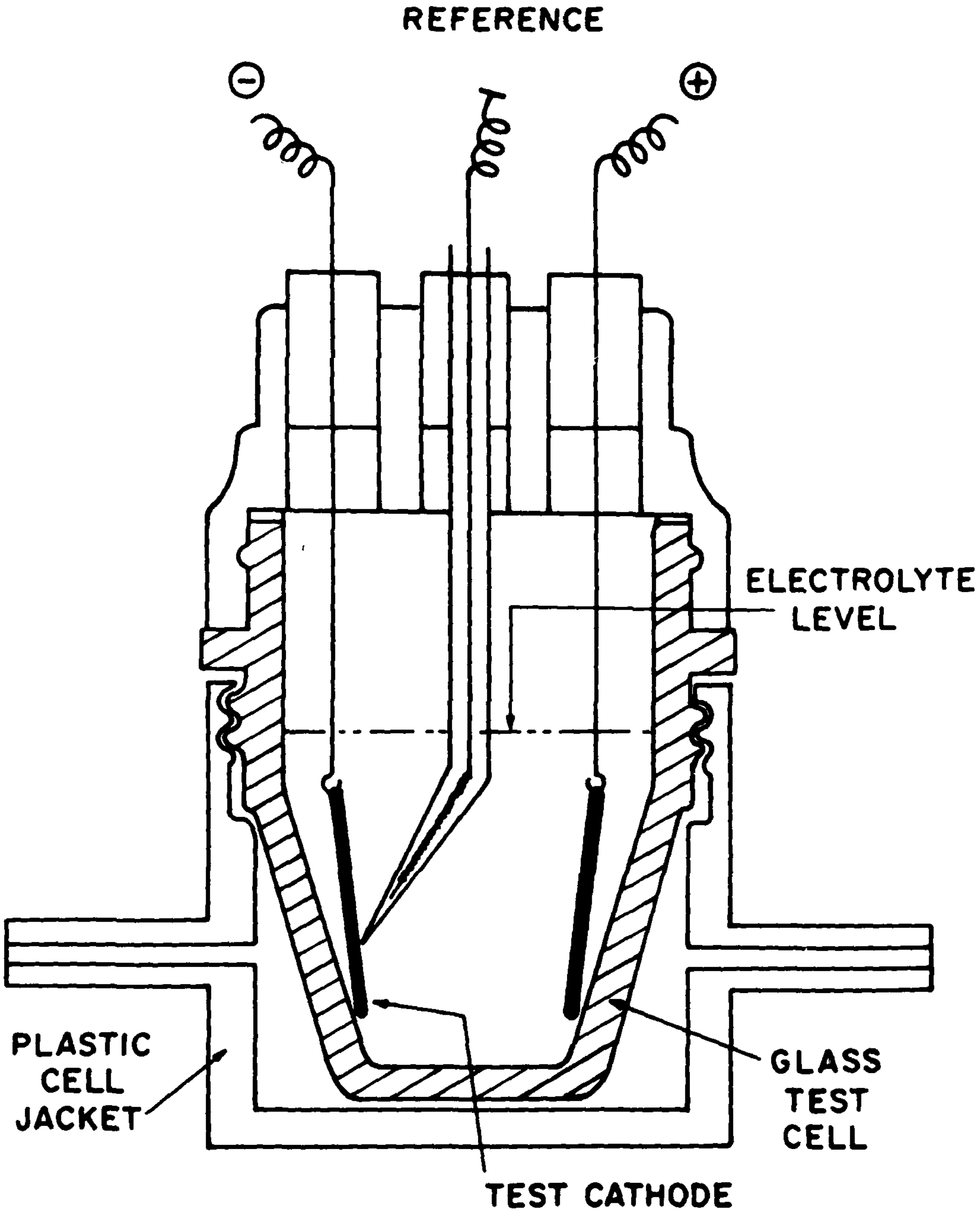

FIGURE 1. Eco Test Cell

intervals, until the cut-off voltage was reached (2.5 V).

2.5 Long-Term Tests

Long-term catalyst stability was determined by soaking cathodes for extended periods in dry thionyl chloride containing 1.8 M $LiAlCl_4$, and then carrying out the standard polarization evaluation test described in Section 2.3.

2.6 Anode Performance

During cathode evaluation, anode voltaic performance was evaluated, based on comparison with the reference electrode when the Luggin capillary tip was held against the anode.

3.0 Catalyst Preparation

3.1 Control Cathodes

Four types of reference cathodes were prepared from the following carbons: carbon black, heat-treated carbon black, platinum-catalyzed carbon black, and phthalocyanine-catalyzed carbon black.

The carbon blacks tested were Vulcan XC-72R (Cabot Corp; 9-36H) and Shawinigan Acetylene Black (Shawinigan Corp. 50% C; 9-36C). These carbon blacks were also evaluated after they had been heat-treated for one hour under argon (9-36B and 9-36A respectively).

The platinum-catalyzed carbon black (2-160) was 10% platinum on carbon (120 - 150 m^2/g) obtained from Prototech Inc. (Newton Upper Falls, MA).

Two metallated phthalocyanine-catalyzed carbons were prepared by dissolving 35 mg of the iron (2-159) or cobalt (2-158) phthalocyanine in 100 ml THF and then soaking a 5 cm^2 (75 mg carbon) prepared cathode (9-36H) in the solution to adsorb the catalyst; the resultant loading of catalyst was approximately 5% (0.7 mg catalyst/cm^2).

3.2 ECO Catalysts

Three types of catalysts were prepared: TAA catalyst admixed with carbon, TAA catalyst admixed with carbon and heat-treated, and TAA catalyst covalently bonded to the carbon surface.

The admixed catalysts were prepared by physically mixing the TAA with the carbon in known weight ratios. The resulting mixture was then used as the carbon in cathode fabrication (Section 2.1).

The heat-treated catalyzed carbons were prepared by heating the admixed catalysts under an argon atmosphere for one hour. The resulting mixture was then used as the carbon in cathode fabrication (Section 2.1).

The covalently bonded catalyzed carbons were prepared by heating for one hour under argon a known weight ratio of TAA with a carbon to which TAA was covalently bonded via an alkyl chain. The resulting mixture was then used as the carbon in cathode fabrication (Section 2.1).

3.3 Chemical Preparation Techniques

3.3.1 Controls

The iron phthalocyanine (2-159) was obtained from Alfa Products (Danvers, MA); the cobalt phthalocyanine (2-158) was obtained from Eastman Kodak Co. (Rochester, NY). These organometallics were used directly without additional purification or heat treatment.

3.3.2 TAAs

The metallated tetraazannulenes (TAAs) were prepared by reacting one equivalent of metal acetate and one molar equivalent of diamine in one volume of 1:1::ethanol:methanol with one molar equivalent of freshly prepared aldehyde[8]. The solution was held at reflux for 30 minutes with stirring; upon cooling, the metallated product was obtained by filtration.

3.3.3 Bonded TAAs

The bonded TAAs were prepared by reacting five molar equivalents of bis-N,N-dimethyl-amino TAA with one molar equivalent of chloro-alkylated Vulcan XC-72R for 48 hours in sulfolane at 100°C under nitrogen. The resulting covalently bonded TAA was metallated by reaction with ten equivalents of metal acetate in sulfolane at 100°C under nitrogen for 48 hours. This bonding procedure provided bonded TAA levels with an average loading of 3% by weight based on elemental analysis. The bonded-TAA carbon was then mixed with TAA to provide the catalyzed cathodes tested in this program (9-18 for FeTAA and 9-26 for CoTAA).

The bis-N,N-dimethyl-amino TAA was prepared by reacting sublimed TAA with 2.1 molar equivalents of dimethylamine hydrochloride and 2.1 molar equivalents of paraformaldehyde in 20 weight volume equivalents of dioxane at reflux for 30 minutes. Following removal of the solvent, the functionalized TAA was obtained by column chromatography on aluminum oxide (Woehm basic grade 1) in methanol.

The chloroalkylated Vulcan XC-72R was obtained by reaction of the carbon with an equal weight of 1-chloro-4-iodobutane and a tenth weight of anhydrous aluminum trichloride in ten weight equivalents of freshly distilled nitromethane. The reaction mixture was kept at reflux (101°C) for three days under a nitrogen atmosphere, harvested by centrifugation, and soxhletted in methanol for six days. Elemental analysis showed this chloroalkylated carbon to contain 0.09 mM chlorine/g.

Previous work by ECO showed this alkyl bonded TAA to be stable in 150°C 85% phosphoric acid[9].

4.0 Cathode Evaluation

4.1 Cathode Performance

A number of TAA-catalyzed cathodes (0.5 cm^2), as well as carbon, phthalocyanine-catalyzed and platinum-catalyzed controls, were evaluated. All data obtained were IR-free and were recorded while the load was increased over a period of ten minutes. The electrolyte (dry 1.8 M $LiAlCl_4$), the anode, the Shawinigan Acetlyene Black (SAB), and the reference electrode were all materials commercially used. The tests were carried out in a glove box under a dry air atmosphere.

4.1.1 Performance as a Function of Carbon

The effect of the cathode carbon support on cathode performance is shown in Table 1, based on cathodes prepared with 5% PTFE. Shawinigan Acetlyene Black (9-36A) and Vulcan XC-72 (9-36B), when heat-treated, have approximately equal performance in the load range of 10 to 100 mA/cm^2. When these two carbons are catalyzed with 10% TAA (9-32C and 9-32F respectively), this performance improves significantly to where performance at 100 mA/cm^2 is equal to or better than that for the neat carbons at 10 mA/cm^2 (ie.: factor of 10 performance improvement).

Table 1

Performance as a Function of Carbon Type
(5% PTFE; 10% catalyst level)

Catalyst	Carbon		Cathode Performance*, V		
		Load, mA/cm^2:	10	50	100
9-32F	Vulcan XC-72R		3.505	3.345	3.205
---	Vulcan XC-72R (9-36B)		3.298	3.195	3.105
9-32C	Shawinigan 50% C		3.515	3.468	3.420
---	Shawinigan 50% C (9-36A)		3.320	3.195	3.120

* Cathode Performance measured vs Li reference (IR-free)

Provided in Figure 2 is a graphical display of the effect of a second TAA catalyst (9-22F) on Vulcan XC-72R cathode performance. This catalyst improved carbon cathode performance by over a factor of ten in the load range of 10 - 100 mA/cm^2; cathode performance of 9-22F is still over 3.0 V at loads over 250 mA/cm^2.

4.1.2 Performance as a Function of PTFE Content

The effect of PTFE content on cathode performance is shown in Table 2, based on heat-treated Shawinigan Acetylene Black containing two different TAA levels (10%, 9-32C; 1%, 9-32A). These data are not conclusive other than to observe that varying PTFE content over the range of 5 to 30% by weight does not diminish the catalytic effect of the TAAs.

4.1.3 Performance as a Function of Catalyst Content

The effect of TAA catalyst loading on cathode performance is shown in Table 3, based on heat-treated Shawinigan Acetylene Black (5% PTFE) containing TAA at levels of 0 to 33% by weight. There appears to be an optimum catalyst loading at approximately 10% TAA. Higher TAA loadings negatively affect performance, probably because TAA is non-conductive and increased loadings may increase ohmic overpotential.

4.1.4 Performance as a Function of Metal Center

The effect of the metal center in the organometallic catalyst (TAA) on cathode performance is shown in Table 4, based on cathodes prepared with heat-treated Vulcan XC-72R (5% PTFE) containing approximately 33% catalyst by weight. Cobalt and iron are shown to be preferred metal centers over nickel.

4.1.5 Performance as a Function of TAA Type

The effect of TAA type on catalyzed cathode performance is

FIGURE 2. Polarization Characteristics of Cathode in Li/SOCl$_2$

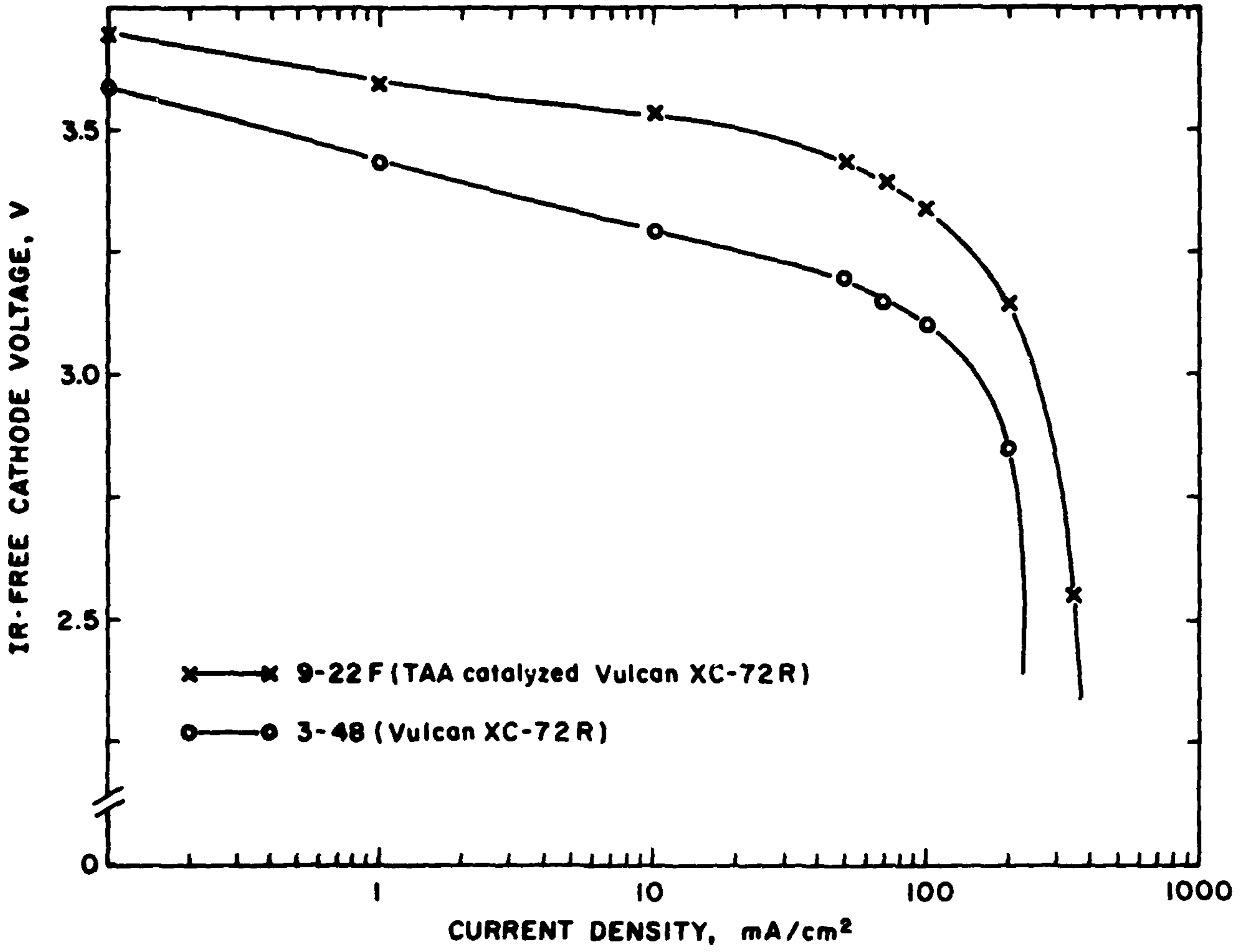

Table 2

Cathode Performance as a Function of PTFE Content

Catalyst	PTFE, %		Cathode Performance*, V		
		Load, mA/cm^2:	10	50	100
9-32C	5		3.515	3.468	3.420
9-32C	30		3.480	3.383	3.288
9-32A	5		3.355	3.235	3.115
9-32A	30		3.370	3.248	3.180

* Cathode Performance measured vs Li reference (IR-free)

Table 3

Cathode Performance as a Function of Catalyst Content (5% PTFE)

Catalyst	% Catalyst, %		Cathode Performance*, V		
		Load, mA/cm^2:	10	50	100
9-36A	0		3.320	3,195	3.090
9-32A	1		3.355	3.233	3.115
9-32B	5		3.470	3.235	---
9-32C	10		3.515	3.468	3.420
9-32D	20		3.494	3.338	---
9-32E	33		3.443	3.383	3.330

* Cathode Performance measured vs Li reference (IR-free)

Table 4

Cathode Performance as a Function of Metal Center in TAA
(5% PTFE; 33% catalyst level)

Catalyst	Metal Center	Cathode Performance*, V		
	Load, mA/cm^2:	10	50	100
9-27D	Co	3.540	3.460	3.400
9-27B	Fe	3.465	3.352	3.253
9-22B	Ni	3.290	3.220	0.800

* Cathode Performance measured vs Li reference (IR-free)

shown in Table 5, based on cathodes prepared with heat-treated Vulcan XC-72R (5% PTFE) containing approximately 33% catalyst by weight. The bonded TAAs (9-26 and 9-18) are shown to be active catalysts, especially at low loads. All of the TAAs tested are shown to be active catalysts.

4.1.6 Performance after Long-Term Test

The effect of soaking the catalyzed cathodes in the thionyl chloride electrolyte on cathode performance is shown in Table 6, based on cathodes prepared with Vulcan XC-72R (5% PTFE) containing either 5% TAA (9-32B) or 5% iron phthalocyanine (2-159). Cathode performance of carbons catalyzed with TAA is not shown to degrade after 720 hours; carbons catalyzed with phthalocyanine are shown to degrade significantly.

4.1.7 Summary of Performance Tests

Carbons catalyzed with the TAAs were shown to provide significantly improved cathode performance over both neat carbon and carbon catalyzed with phthalocyanines. Three different TAA types, as well as TAA covalently bonded to the carbon, were shown to be active cathode catalysts. Long-term soaking in the electrolyte did not affect TAA catalytic performance.

During the Phase I program, a number of variables affecting catalyst performance were identified. These include carbon type, PTFE content, catalyst content, metal center, and catalyst chemistry. The initial information obtained showed the TAAs to be active cathode catalysts over a wide range of conditions; further work will be required to identify the characteristics of an optimal catalyzed cathode and then to prepare and test the optimal catalyst.

Table 5

Cathode Performance as a Function of TAA Catalyst Type
(5% PTFE; 33% catalyst level)

Catalyst	Metal Center	Cathode Performance[1], V		
	Load, mA/cm^2:	10	50	100
9-27D	Co	3.540	3.460	3.400
9-27A	Fe	3.523	3.473	3.420
9-23A	Co	3.500	3.400	3.330
9-24C	Fe	3.497	3.432	3.367
9-26	Co	3.442	3.155	2.852
9-18	Fe	3.445	3.140	2.880
9-22F	Co	3.530	3.443	3.340[2]

1. Cathode Performance measured vs Li reference (IR-free)

2. At a load of 350 mA/cm^2, performance of 2.525

Table 6

Cathode Performance after Long-Term Test as a Function of
Catalyst Type (5% PTFE; 5% catalyst level)

Catalyst	Time, hrs	Cathode Performanace*, V		
	Load, mA/cm^2:	10	50	100
9-32B	0	3.470	3.235	---
9-32B	720	3.493	3.395	3.285
2-159 (FePc)	0	3.485	3.280	3.128
2-159 (FePc)	768	3.330	3.095	2.885

* Cathode Performance measured vs Li reference (IR-free)

4.2 Cathode Capacity

A small number of TAA-catalyzed cathodes (0.5 cm^2) were evaluated; all data were taken at constant load (20 mA/cm^2) and the time at this load, until the cut-off voltage (2.5 V) was reached, recorded. The test conditions were identical to those used in the cathode performance studies (Section 4.1). The general shape of the cathode discharge curve is provided in Figure 3 for TAA-catalyzed (9-36E) and uncatalyzed (9-36G) carbons.

4.2.1 Capacity as a Function of Carbon

The effect of the cathode support carbon on TAA-catalyzed cathode capacity is shown in Table 7, based on cathodes prepared with 5% PTFE and 10% TAA. Catalyzed Shawinigan Acetylene Black (9-36E) is shown to provide capacity significantly improved over catalyzed Vulcan XC-72R (9-36C). Cathode capacities, on the order of 3 Ah/g carbon, were observed for both catalyzed carbons which are significantly higher (factor of 3) than literature reports for either neat carbon[5] or phthalocyanine-catalyzed carbon[7] at comparable discharge rates (20 mA/cm^2).

4.2.2 Capacity as a Function of PTFE Content

The effect of PTFE content on TAA-catalyzed cathode capacity is shown in Table 8, based on cathodes prepared with heat-treated Shawinigan Acetylene Black containing two different TAA levels (10%, 9-32C; 1%, 9-32A). These data do not conclusively show a trend other than to suggest that varying the cathode PTFE content over the range of 5 to 30% by weight does not reduce the capacity of TAA-catalyzed cathodes (ie.: over 3 Ah/g catalyzed carbon).

4.2.3 Capacity as a Function of Catalyst Content

The effect of TAA-catalyst load on cathode capacity is shown

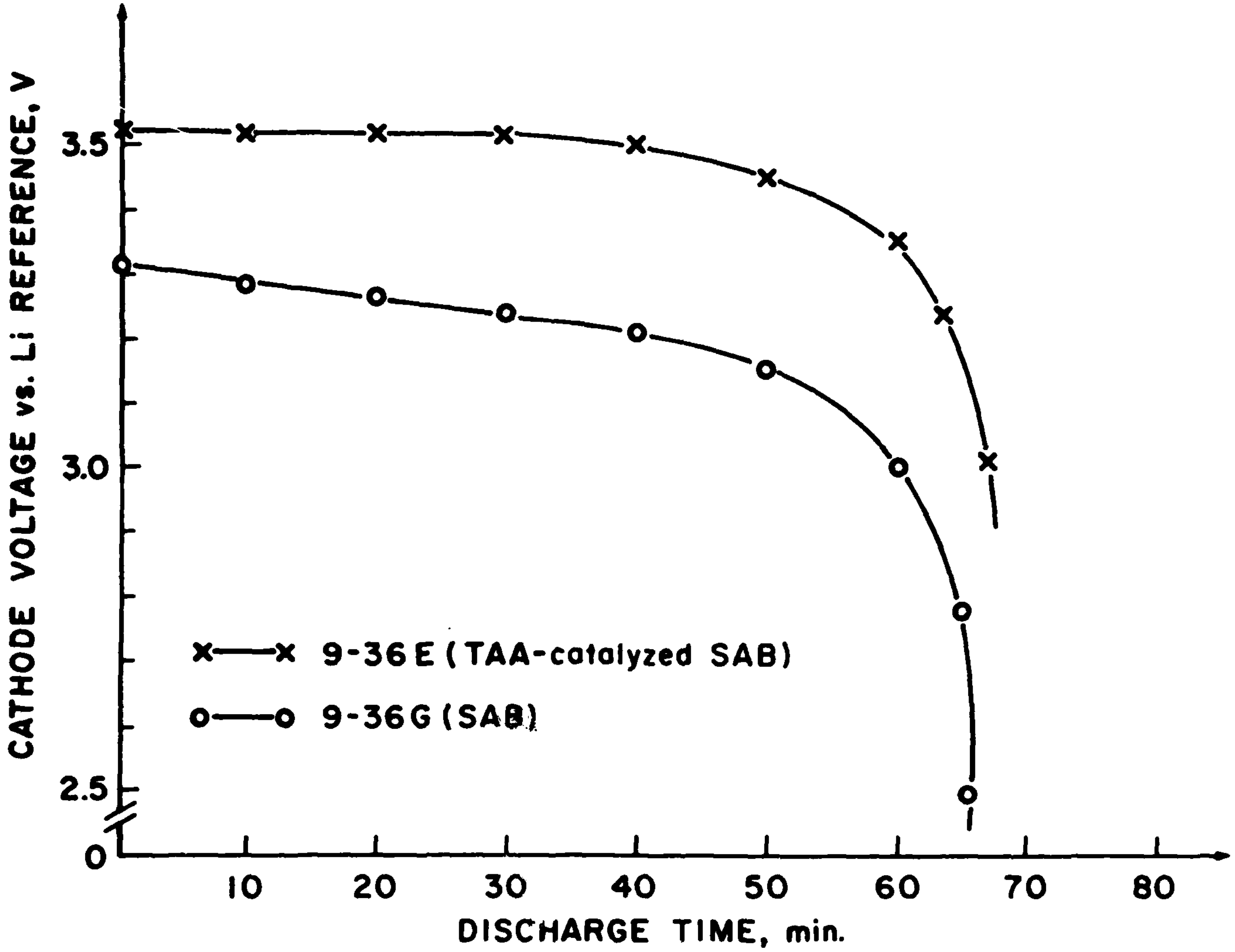
FIGURE 3. Discharge Characteristics of Cathode in $Li/SOCl_2$ @20 mA/cm²

Table 7

Effect of Carbon Type on Cathode Capacity
(5% PTFE; 10% catalyst level)

Catalyst	Carbon	Average Cell Voltage[1], V	Discharge Time[2], min.
9-36E	Shawinigan 50% C	3.50	67
9-36C	Vulcan XC-72R	3.24	58

1. Cathode voltage vs Li reference at 50% depth of discharge
2. Time at 20 mA/cm^2 to cut-off voltage of 2.5 V

Table 8

Effect of PTFE Content on Cathode Capacity

Catalyst	PTFE, %	Average Cell Voltage[1], V	Discharge Time[2], min.
9-32C	5	3.41	58
9-32C	30	3.49	56
9-32A	5	3.30	58
9-32A	30	3.29	70

1. Cathode voltage vs Li reference at 50% depth of discharge
2. Time @ 20 mA/cm^2 to cut-off voltage of 2.5 V

in Table 9, based on heat-treated Shawinigan Acetylene Black (5% PTFE) containing TAA at levels of 1 to 33% by weight. Varying catalyst load does not appear to affect cathode capacity; both power and energy densities are increaased, based on the observed increase in average cell voltage (voltage at 50% depth of discharge), at catalyst loads over 10%.

4.2.4 Capacity as a Function of TAA Type

The effect of TAA type on cathode capacity is shown in Table 10. The first TAA catalyst (9-24C) showed significantly improved discharge time, but the voltaic performance was poor. The other two types of TAAs (9-32A and 9-36E) gave comparable capacities, although there was a measurable difference in average cell voltage. These results show that significant improvements in cathode capacity are possible by optimizing the TAA catalyst to have a combination of the desirable properties of 9-24C and 9-36E. Based on the results obtained, a further doubling of cathode capacity, to over 6 Ah/g catalyzed carbon, is possible.

4.2.5 Capacity after Long-Term Test

The effect on cathode capacity of soaking a TAA-catalyzed cathode (9-32A) in the thionyl chloride electrolyte is shown in Table 11. Due to the brevity of the Phase I research program, it was not possible to carry out extensive long-term capacity studies. The results obtained showed a decrease in capacity over the 30 day stress period. During this period, the cathode was also observed to structurally change; the source of the observed capacity decay may not be due to catalyst decay.

4.2.6 Summary of Capacity Test

Carbons catalyzed with the TAAs were shown to have significantly improved performance over both neat carbon or carbon

Table 9

Effect on Cathode Capacity of Varying Catalyst Content
(5% PTFE)

Catalyst	% Catalyst, %	Average Cell Voltage[1], V	Discharge Time[2], min.
9-32A	1	3.30	58
9-32C	10	3.41	58
9-32E	33	3.42	58

1. Cathode voltage vs Li reference at 50% depth of discharge
2. Time @ 20 mA/cm^2 to cut-off voltage of 2.5 V

Table 10

Effect of Catalyst Type on Cathode Capacity
(5% PTFE)

Catalyst	Average Cell Voltage[1], V	Discharge Time[2], min.
9-24C	0.54	120 [3]
9-36E	3.50	67
9-32A	3.29	70

1. Cathode voltage vs Li reference at 50% depth of discharge
2. Time @ 20 mA/cm^2 to cut-off voltage of 2.5 V
3. Cut-off voltage not used

Table 11

Cathode Capacity after Long-Term Test of Catalyst 9-32A (30% PTFE)

Stress Time, hr	Average Cell Voltage[1], V	Discharge Time[2], min.
0	3.29	70
720	3.22	55

1. Cathode voltage vs Li reference at 50% depth of discharge
2. Time @ 20 mA/cm^2 to cut-off voltage of 2.5 V

catalyzed with phthalocyanines (Table 12). Improvements in cathode capacity, on the order of a factor of three (Ah/g carbon mix), were observed. Long-term soaking in the electrolyte reduced cathode capacity by 20%; the stressed cathode still had capacity a factor of two greater than reported values[5,7].

During the Phase I program, a number of variables affecting cathode capacity were identified. These include carbon type, PTFE content, catalyst load, and catalyst type. Significant further improvements in cathode capacity appear possible based on results obtained.

4.3 Anode Performance

No extensive data were taken but, based on comparison of anode voltaic performance vs the Li reference, no data were obtained which showed the anode to be significantly affected by being in electrolytes containing carbons catalyzed by TAAs.

5.0 Conclusions

ECO prepared and tested a number of new organometallics as cathode catalysts for Li/$SOCl_2$ batteries. Excellent cathode performance (factor of 10 improvement) and cathode capacity (factor of 3 improvement) were observed for low catalyst loads compared to recent literature values for carbon or phthalocyanine-catalyzed carbon. The mechanisms for these improvements could not be determined based on the results obtained, but they probably result from a lowering in the carbon activation potential and a change in the cathode reaction mechanism. Such a change in reaction mechanism may result in a safer Li/$SOCl_2$ battery system through reduced formation of unstable reaction by-products.

6.0 Recommendations

ECO recommends that future work be focused on six areas:

Table 12

Comparison of Cathode Capacity Data of TAAs with Literature Values

Catalyst	Cathode Capacity, A-h/g @ 20 mA/cm^2
9-32A	3.3
9-36E	3.2
SAB[1]	0.65
CoPc[1]	0.75
FePc[1]	1.2
SAB[2]	1.2

1. From Doddapaneni, Ref. 7 (1982)
2. From Dey, Ref. 5 (1979)

catalyst optimization, matrix and electrode development, performance/cost studies, mechanistic studies, hardware preparation and testing, and battery production for evaluation in Army programs. These areas will form the basis for a Phase II proposal and are briefly summarized below.

6.1 Catalyst Optimization

Under the Phase I program, ECO made no attempt to optimize cathode performance or capacity. Further work is required to obtain parametric data on the effect of TAA type, catalyst content and carbon type on cathode performance, cathode capacity and rate of formation of unstable reaction by-products as a function of discharge rate and cell temperature. Other parametric studies should include evaluation of shelf-life and voltage delay effects (Li passivation).

6.2 Matrix and Electrode Development

The cathodes tested in Phase I were produced following techniques drawn from ECO's experience with wet-proofed fuel cell cathodes. Research is needed to adapt this cathode structure (carbon support, current collector) and component concentrations (PTFE, carbon catalyst) to optimize Li/$SOCl_2$-system cathode performance. While the present methods used in cathode fabrication already show TAA-catalyzed carbons to be superior to all previous catalyzed and uncatalyzed carbons, even better cathode performance may be obtained with structures designed for use specifically with TAA-catalyzed carbons.

6.3 Performance/Cost Studies

Methods to reduce catalyst production costs or estimates of production costs on any scale were not considered in Phase I. For example, the covalently bonded catalyst is more expensive to produce than the admixed catalyst, but the bonded catalyst may provide batteries with extended shelf-life. Such trade-offs should be examined as more information becomes available on catalyzed cathode characteristics and on matrix requirements.

6.4 Mechanistic Studies

The safety of Li/$SOCl_2$ batteries may be improved by using TAA-catalyzed carbons because of their effect on the cathode reaction mechanism. Lower rates of heat generation and of unstable reaction by-product generation may be obtained. The reaction mechanisms on TAA-catalyzed cathodes should be evaluated using four techniques familiar to ECO: spectroelectrochemistry[10] and cyclic voltammetry[11] of the partially reacted $SOCl_2$, differential thermal analysis[4] of the electrolyte in the presence of the high-rate TAA-catalyzed carbons, and AC impedence measurements, with respect to depth of discharge and shelf-life, to evaluate the effect of the TAA catalysts on lithium chloride film formation and resistance.

6.5 Hardware Preparation and Testing

During Phase I, ECO attempted to have C-cells made by Battery Engineering Inc. (BEI) with cathodes catalyzed with TAA-carbon mixtures. Due to time constraints, the effort failed because BEI was unable to fabricate cathodes using its conventional techniques. Work should be carried out to solve the practical problems of working with a material of different mechanical properties, and C-cells prepared using the optimized TAA-catalyzed carbons. Parametric studies to provide performance characteristics, including shelf-life and voltage delay effects as a function of discharge rate and operating temperature, should be performed.

6.6 Battery Production

The purpose of the Phase I/Phase II programs is to provide the Army with useful, safe batteries at a reasonable cost. The $Li/SOCl_2$ battery, showing optimum performance, should be produced in sufficient numbers and provided to the Army for testing in various applications. Evaluation of the field data obtained will determine the true value of any new $Li/SOCl_2$ battery system.

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Dr. M. Walsh and Mr. R. S. Morris of ECO provided expert technical advice and supervision under this program. Battery Engineering Inc. kindly provided samples of the electrolyte, the lithium anode and the SAB.

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Appendix A

List of Cathodes Tested

Code	Description
2-158	5% Cobalt phthalocyanine on Vulcan XC-72R
2-159	5% Iron phthalocyanine on Vulcan XC-72R
2-160	10% Pt on Carbon (120 - 150 cm^2/g)
9-18	Iron TAA mixed 1/2 with iron TAA bonded to Vulcan XC-72R and then heat-treated at 500°C
9-22B	Nickel tetramethyl TAA mixed 1/2 with Vulcan XC-72R and heat-treated at 550°C
9-22F	Cobalt tetramethyl TAA mixed 1/2 with Vulcan XC-72R and heat-treated at 950°C
9-23A	Cobalt bis-azophenyl TAA mixed 1/2 with Vulcan XC-72R and heat-treated at 700°C
9-24C	Iron bis-azophenyl TAA mixed 1/2 with Vulcan XC-72R and heat-treated at 850°C
9-26	Cobalt TAA mixed 1/2 with cobalt TAA bonded to Vulcan XC-72R and then heat-treated at 500°C
9-27A	Iron TAA mixed 1/2 with Vulcan XC-72R and heat-treated at 900°C
9-27B	Iron TAA mixed 1/2 with Vulcan XC-72R and heat-treated at 550°C
9-27D	CoTAA mixed 1/2 with Vulcan XC-72R and heat-treated at 950°C
9-32A	Cobalt TAA mixed 1/100 with SAB and heat-treated at 950°C
9-32B	Cobalt TAA mixed 1/20 with SAB and heat-treated at 950°C
9-32C	Cobalt TAA mixed 1/10 with SAB and heat-treated at 900°C
9-32D	Cobalt TAA mixed 1/5 with SAB and heat-treated at 950°C

9-32E	Cobalt TAA mixed 1/2 with SAB and heat-treated at 950°C
9-32F	Cobalt TAA mixed 1/10 with Vulcan XC-72R and heat-treated at 950°C
9-36A	Shawinigan Acetylene Black 50% C heat-treated at 950°C
9-36B	Vulcan XC-72R heat-treated at 950°C
9-36C	CoTAA mixed 1/10 with Vulcan XC-72R
9-36E	CoTAA mixed 1/10 with SAB
9-36G	Shawinigan Acetylene Black 50% C (SAB)
9-36H	Vulcan XC-72R