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EFFECT OF R GROUPS ON NA/RSSR BATTERY CHARACTERISTICS

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## EFFECT OF R GROUPS ON Na/RSSR BATTERY CHARACTERISTICS

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Advanced secondary batteries operating at intermediate temperatures, i.e. 100 to 200°C, have attracted considerable research interest due to their inherent advantages over higher temperature systems such as the Na/S or Li/FeS<sub>2</sub> batteries. Current work in this laboratory has involved research on a novel class of intermediate temperature batteries based on a concept similar to the sodium/beta"-alumina/sulfur battery, but operating within the range of 100 to 150°C, and having an organosulfur positive electrode (1). The organosulfur electrodes are based on the reversible, electrochemical two electron reduction of the organo-disulfide to the corresponding thio anion,



where R is an organic moiety. The oxidation of thiols to disulfides has been long established, but has not been considered previously in the context of energy conversion. The attraction of such a generic organic redox couple for battery research is the ability to tailor the physical, chemical, and to a lesser extent electrochemical properties of the molecule through choice of the organic moiety. The viscosity, liquidus range, dielectric constant, equivalent weight, and redox potential, of the organosulfur electrodes can in fact be varied in a predictable manner.

## EXPERIMENTAL

Methyl disulfide, Gold Label (Aldrich), was used without further purification. Phenyl disulfide (Aldrich), was recrystallized from ethanol prior to use. Difluorophenyl disulfide was made from the oxidation of 4-fluorothiophenol (Aldrich) by iodine in water, and subsequently extracted with petroleum ether, and finally distilled under reduced pressure. Dipentafluorophenyl disulfide was similarly made from pentafluorothiophenol (Aldrich), which was purified by recrystallization from ethanol. Ethoxyethyl disulfide and Methoxyethyl disulfide were made by the reaction of 2-chloroethyl ethyl ether and 2-chloroethyl methyl ether with potassium hydrogen sulfide in methanol under pressure to yield the corresponding mercaptan; the  $\beta$ -ethoxy-alkyl mercaptans were fractionally distilled and the purified mercaptans oxidized to the disulfides which were distilled under reduced pressure prior to use. Transition metal phthalocyanines (Pfaltz and Bauer) were used as is. All solvents were obtained from Aldrich and stored over molecular sieves in an argon atmosphere dry box prior to use.

Beta"-alumina tubes ( 10 cm x 1 cm, .8 mm wall ) were filled with highly purified sodium metal (2), sealed with high temperature epoxy to an aluminum cap through which a stainless wire contacted the sodium metal electrode. The beta"-alumina tube/sodium electrode was tightly wrapped in graphite felt and inserted into a stainless steel cell yielding approx-imately 20 cm<sup>2</sup> of electrolyte surface area. The cell was sealed with silicone o-rings, and fitted with a transducer to monitor the internal pressure of the positive electrode. All cells were subsequently cycled galvanostatically under computer control using a IBM PC/AT with a Data Translation 2801-A data aquisition card, interfaced to a PAR 373 Potentiostat/ Galvanostat, and an Omega PX600 pressure transducer.

## RESULTS

The theoretical energy density of a Na/CH<sub>3</sub>SSCH<sub>3</sub> cell is 770 Whrs/Kg if the organosulfur electrode is used without solvents. Solubility studies indicated that an approximate weight ratio of DMSO to dimethyl disulfide ( DMDS ) of 3 to 1 was sufficient to completely dissolve the sodium thiomethoxide generated on cell discharge at the cell temperature of 110°C. Accordingly, positive electrodes were assembled using a range of 30% to 80% solvent to facilitate cell discharge. Open circuit voltage of the Na/DMDS cells ranged from 2.0 to 1.8 volts; discharge rates were 10 mA/cm<sup>2</sup> at 1.2 volts to 100% of available capacity, and recharged at 10 mA/cm<sup>2</sup> at an average of 2.4 volts to 95% of capacity. The addition of an electrocatalyst, cobalt phthalocyanine ( CoPc ), boosted the charge/discharge rates by a factor of five. Na/DMDS cells having 1 wt% CoPc were able to discharge at 50 mA/cm<sup>2</sup> for over 50% of available capacity ( fig. 1 ) corresponding to a power density of 25 W/Kg, and charge rates of approximately 20 mA/cm<sup>2</sup>. The cells could be cycled up to three times before excessive internal pressure led to cells leaks. The pressure increase was attributed to slow chemical reduction of DMSO by thiomethoxide to yield CH<sub>3</sub>SCH<sub>3</sub> as well as electrochemical reduction of the solvent. The use of solvents less susceptible to reduction, such as dimethyl sulfone, alleviated this problem.

Positive electrodes were constructed using a series of aromatic disulfides, with 50 % solvent to ensure dissolution of cell products. Sodium/phenyl disulfide cells exhibited open circuit voltages of 2.0 volts and were able to discharge at rates of 7.5 mA/cm<sup>2</sup> at 1.6 volts to 50 % of available capacity. The effect of fluorine substitution on cell performance was dramatic. Sodium/difluorophenyl disulfide cells exhibited open circuit voltages of 2.4 volts and discharged at rates of 10 mA/cm<sup>2</sup> to 90 % of available capacity. Sodium/dipentafluorophenyl di-sulfide cells exhibited open circuit voltages of 3.0 volts, and were capable of similar discharge rates.

Sodium/alkoxyalkyl disulfide cells were assembled and cycled. The effect of incorporation of the ether linkage in the disulfide appeared to be to

increase the solubility of the sodium salts as well as to increase chemical stability of the electrode. The tested cells were able to cycle at 10 to 15 mA/cm<sup>2</sup> to full capacity without pressure increase or evidence of degradation of the solvent.

## CONCLUSIONS

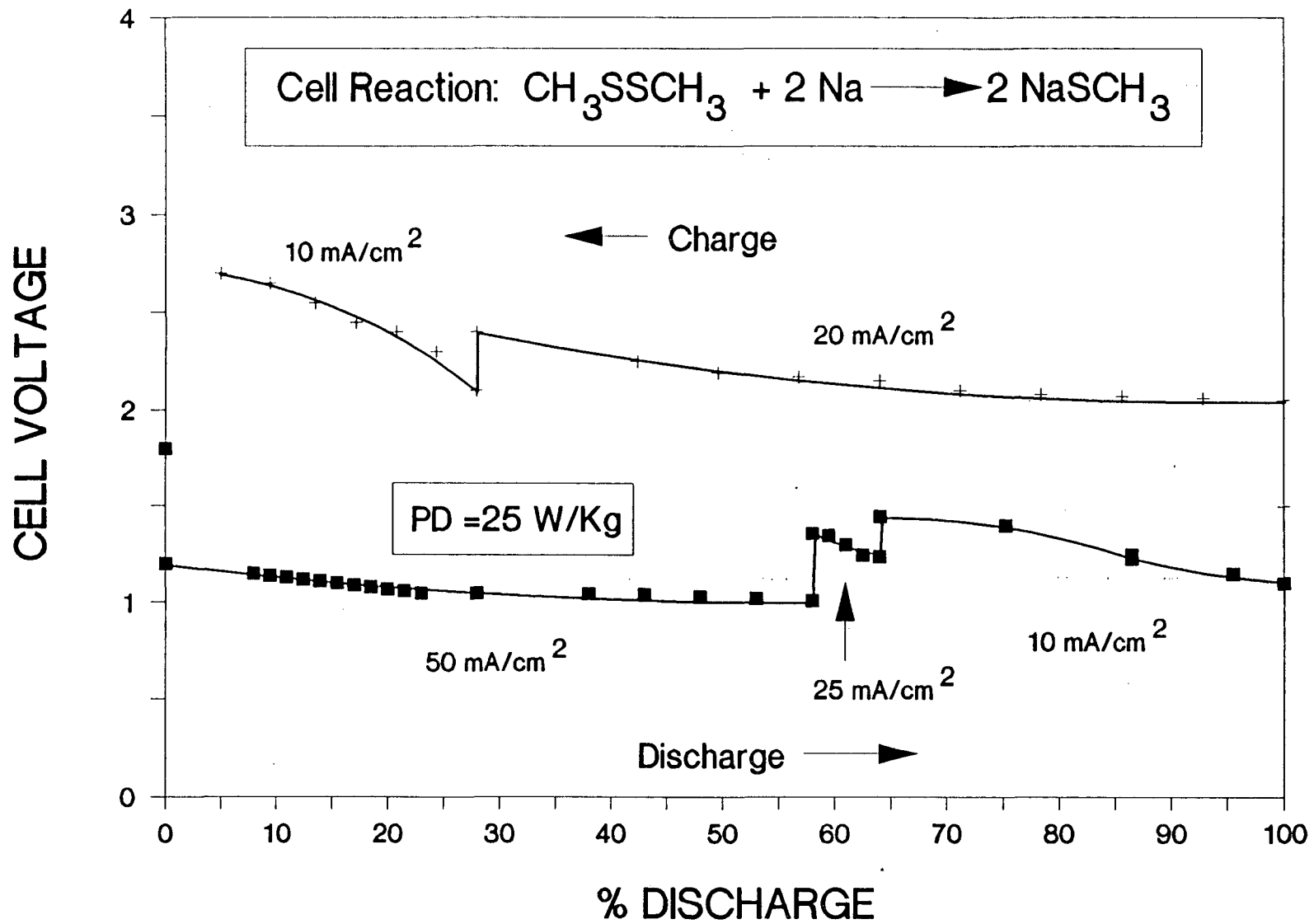
Sodium/organosulfur batteries operating at intermediate temperatures ( 100 to 150° ) can be cycled at high rates, 50 mA/cm<sup>2</sup>, for a fraction of available capacity, and at lower rates, 5 to 10 mA/cm<sup>2</sup> for all of the available capacity. The open circuit voltage of these cells as well as other properties can be manipulated in a predictable manner by choice of the R group in RSSR.

## REFERENCES

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Fig. 1. Charge/discharge behavior of a Na/CH<sub>3</sub>SSCH<sub>3</sub> cell at an operating temperature of 110°C.



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