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NOVEL ELECTROLYTE ADDITIVES TO ENHANCE ZINC ELECTRODE CYCLE LIFE

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Introduction

Electrochemical power sources that utilize zinc electrodes possess many advantages. Zinc is abundantly available, benign, inexpensive, stable over a wide operating temperature range, and has a high oxidation potential. In spite of these advantageous characteristics, rechargeable electrochemical systems based on zinc chemistry have not found widespread use. The major disadvantages of zinc electrodes are that they have limited cycle life due to zinc slumping and zinc electrode shape changes in alkaline solutions resulting from the solubility of zincate ($Zn(OH)_4^{2-}$) in these solutions. As a result, premature cell failure often results due to cell shorting caused by dendritic growth as well as zinc slumping [1,2].

In this paper we describe the chemical and physical characteristics of electrolyte solutions employing additives, particularly for zinc based electrochemical systems. These electrolytes are prepared using the alkali metal salts of 1,3,5-phenyltrisulfonic acid in combination with potassium hydroxide [3]. The alkali metal salts of the acid possess good thermal stability, good ionic conductivity, and have a wide electrochemical voltage window in aqueous systems. With these electrolyte solutions improved cycle life was achieved in Zn/NiOOH and Zn/AgO. Improved cycle life with this additive is attributed to decreased zincate solubility, resulting in reduced zinc slumping and electrode shape changes. In addition, increased shelf-life and reduced self-discharge were also observed in many alkaline power sources.

Experimental

Additives, such as sodium and potassium salts of 1,3,5-phenyltrisulphonic acid were prepared in our laboratory using the standard procedure. All solutions were prepared using deionized water. Potassium

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hydroxide solutions of the desired concentrations were first prepared, and then various amounts of the potassium salt of potassium 1,3,5-phenyltrisulphonate (KPTS) were added to obtain the final desired concentration of salt in 15% and 20% KOH solutions. Saturated solutions of potassium 1,3,5-phenyltrisulphonate in 42% KOH solutions were prepared by vigorously stirring excess potassium 1,3,5-phenyltrisulphonate in 42% KOH at room temperature for 24 hours. This resulted in less than 1% potassium 1,3,5-phenyltrisulphonate in solution. It was found that the solubility of potassium 1,3,5-phenyltrisulphonate decreases with increased concentrations of KOH. Conductivity measurements of solutions were made using a standard liquid conductivity cell having a cell constant of one. Thermal gravimetric analysis were performed using a Perkin Elmer TGA 7 at scan rates of 2°C/min. Electrochemical measurements were performed using a BAS 100A potentiostat and freshly polished glassy carbon electrodes. All measurements were made in deoxygenated solutions. Zn/NiOOH and Zn/AgO cells were built by Westinghouse and Yardney Technical Products, respectively. The solutions used in the Zn/NiOOH cells was composed of either 15% or 20% KOH containing 29% potassium 1,3,5-phenyltrisulphonate, while the Zn/AgO cells were filled with a solution of 42% KOH saturated with potassium 1,3,5-phenyltrisulphonate.

RESULTS AND DISCUSSION

Physical Properties

In Figure 1, the conductivity of potassium 1,3,5-phenyltrisulphonate as a function of concentration is shown. For example, the conductivity of a 1M solution of potassium 1,3,5-phenyltrisulphonate is 0.095 S/cm, as compared to 0.17 S/cm for 1M KOH. Thermogravimetric analysis of sodium 1,3,5-phenyltrisulphonate (NaKPTS) in the presence of oxygen as well as in inert atmospheres was conducted. In Figure 2 is shown the TGA of NaKPTS in an oxygen atmosphere. Finally, its electrochemical behavior was evaluated at a freshly polished glassy carbon electrode, and the linear sweep voltammograms recorded at 50 mV/min is shown in Figure 3. The working range of electrolyte solutions prepared using this salt are as good as many other known salts, and is limited by the oxidation and reduction of water.

Electrochemical Cell Performance

The effect of the presence of potassium 1,3,5-phenyltrisulphonate additive in KOH solutions were evaluated in both Zn/NiOOH and Zn/AgO test cells. The Zn/NiOOH cells (8Ah) were flooded cells and were zinc limited. These cells were filled with electrolytes of either of two compositions: 1) 29% potassium 1,3,5-phenyltrisulphonate in 15% KOH or 2) 29% potassium 1,3,5-phenyltrisulphonate in 20% KOH. These electrolytes have conductivities comparable to the 30% KOH electrolyte (0.61 S/cm) which is commonly used in consumer batteries. The cells were charged at 12.5 mA/cm^2 to 1.89V and discharged at 25 mA/cm^2 to 1.35V. The performance of these cells is shown in Figure 4. After 50 cycles the cell performance started degrading and after 70 cycles the cells were removed from test and physically examined. It was found that the lead wires, which were attached using Pb/Sn solder, had corroded. The leads were reattached using molten Pb. After replacing the separators with new separators the cells were reassembled using the same electrodes, and were then placed back on test. Small amounts of KOH solutions were added in order to wet the new separators. As can be seen in the figure, the cells returned to their original performance after reassembling. After 106 cycles, with minimal loss of capacity, these cells were removed from test and postmortem evaluation performed. A small amount of zinc was found on the bottom of the cell, with no observable shape changes. The electrolyte solutions were analyzed and no degradation products were found.

The additive also was found to help in reducing self-discharge rates. The open circuit loss of cells rated at 8Ah after 120 hours at 24°C is given in Table 1. Average losses of 12% over five days was found. These losses are comparable to nickel-iron, but less than one-half that typically found for nickel-cadmium, nickel-metal hydride, or nickel-zinc cells with 30% KOH solutions.

Table 1. Open circuit loss of Zn/NiOOH cells at 24°C.

cell number	capacity - previous cycle (Ah)	capacity after 120 hrs (Ah)	% loss
1	5	4.4	12%
2	5.1	4.4	14%
3	3.7	3.3	11%
4	3.5	3.1	12%

Three Zn/AgO cells, rated at 12 Ah, were filled with 42% KOH and served as controls. Three Zn/AgO cells were filled with 42% KOH saturated with potassium 1,3,5-phenyltrisulphonate. All of the cells were charged at 0.5A to 2.05 V and discharged at 4 A to 1.1 V. The average performance of these cells is depicted in Figure 5. The cell-to-cell performance variation is found to be very small. As can be seen, the performance of all of the cells are about the same up to 70 cycles. However, at higher cycle numbers the capacity fade rate appears to be smaller for those cells containing the additive. At the present time over 80 cycles have been achieved, and they are continuing to be cycled.

Summary and Conclusions

Novel electrolyte additives were evaluated in Zn/NiOOH and Zn/AgO cells. Initial results indicate enhanced cycle life of these cells. The additive appears to reduce the zinc oxide solubility and thereby increases the zinc electrode cycle life. For example, the solubility of ZnO in 15% KOH is 0.35 M [4], whereas the solubility of ZnO in 15% KOH containing 29% potassium 1,3,5-phenyltrisulphonate is 0.06 M. The additive also seems to be adsorbed onto the surface of the zinc electrode preventing and/ or inhibiting zinc electrode shape changes. The self discharge rate of Zn/NiOOH cells are dramatically reduced in the presence of potassium 1,3,5-phenyltrisulphonate additive. Further experiments are in progress to understand the nature of the interfacial coating and zinc electrode morphology changes with cycle life. The effect of the additive on the cyclic voltammetric behavior at zinc electrodes is being studied.

Acknowledgments

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4. T.P. Dirkse, *J. Electrochem. Soc.,* **115**, 784, (1968).

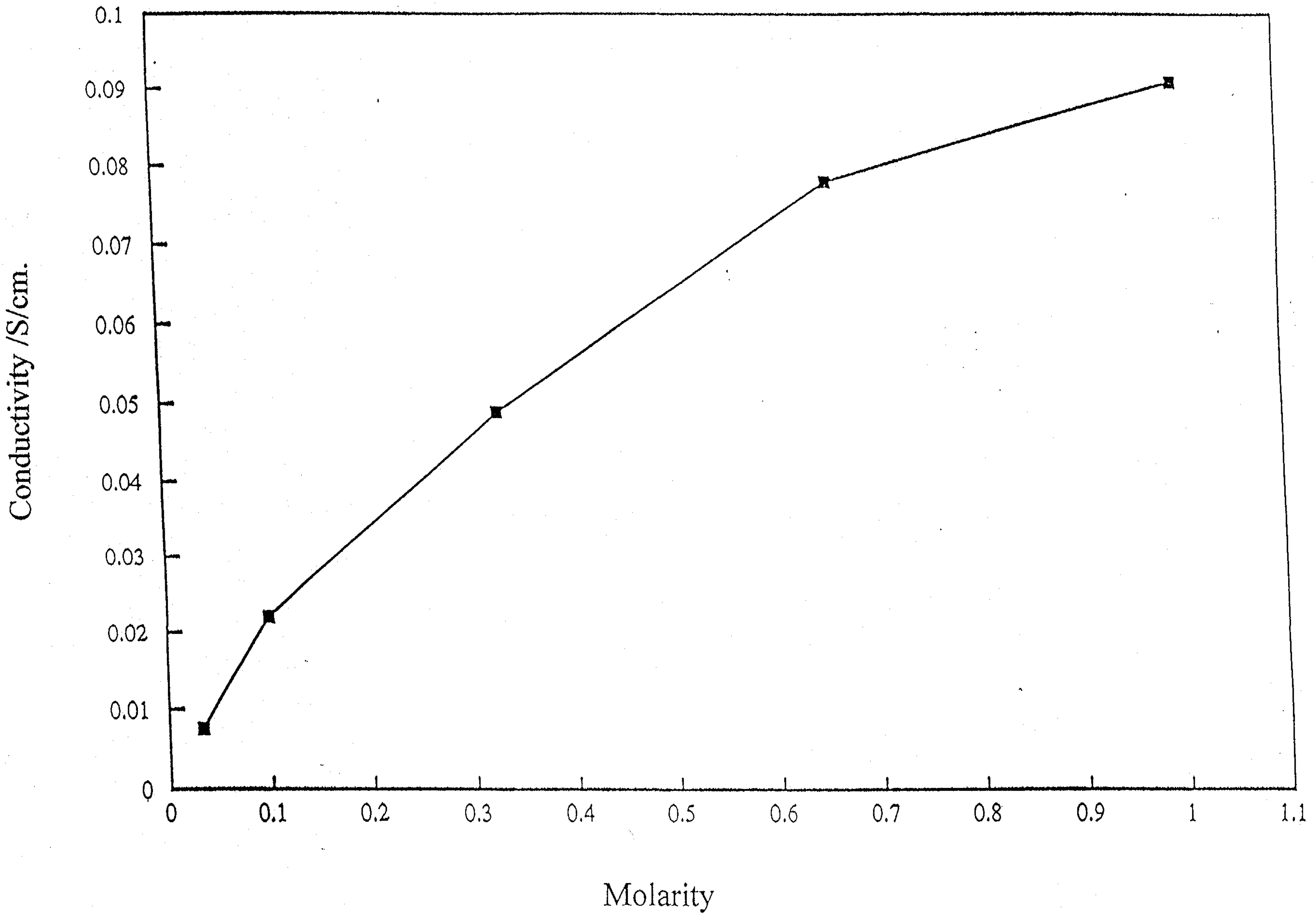

Figure 1. Conductivity of solutions of potassium 1,3,5-phenyltrisulphonate as a function of molarity.

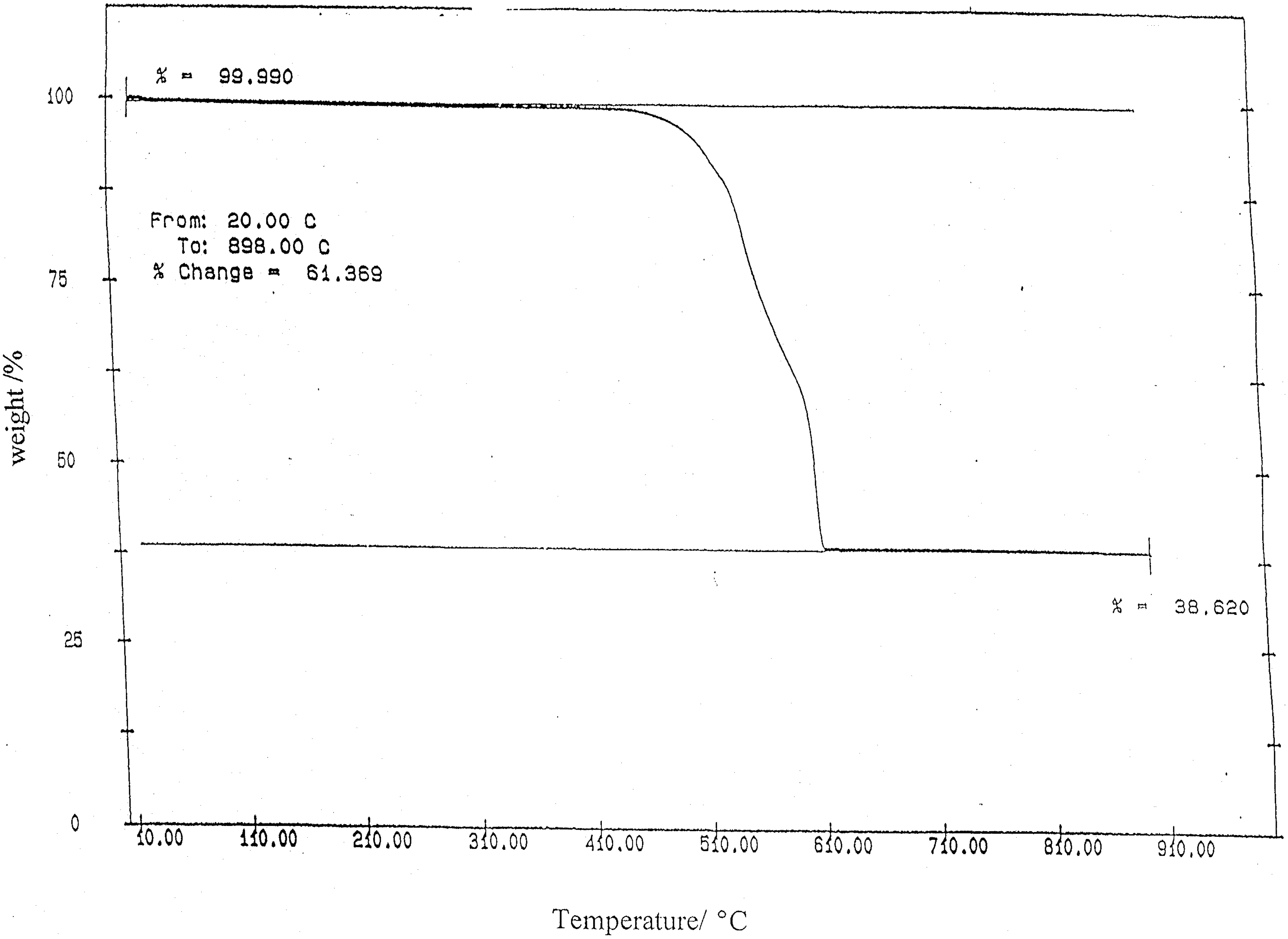

Figure 2. Thermal gravimetric analysis of sodium 1,3,5-phenyltrisulphonate in oxygen at 2°C/min.

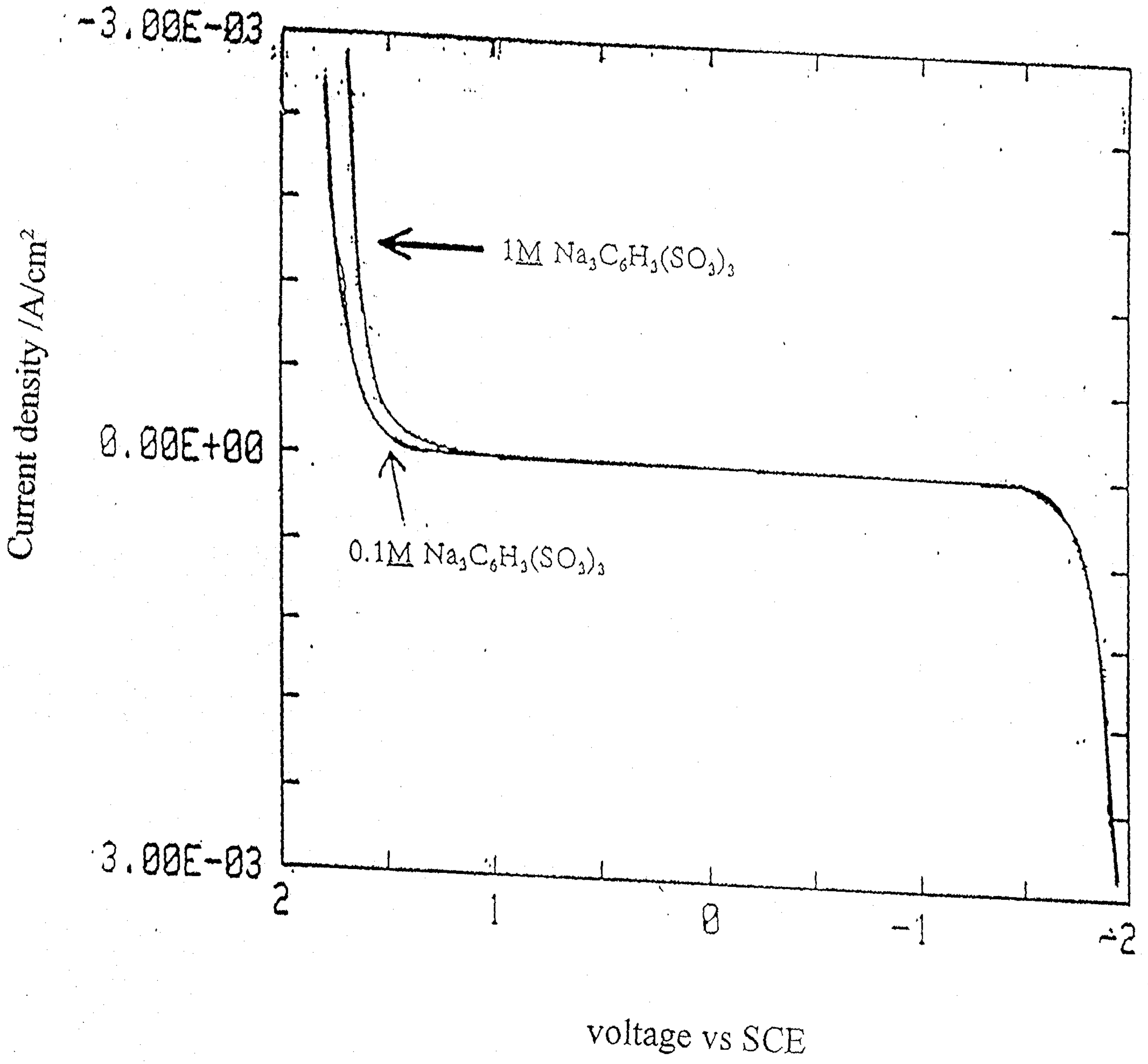

Figure 3. Linear sweep voltammograms of sodium 1,3,5-phenyltrisulphonate.

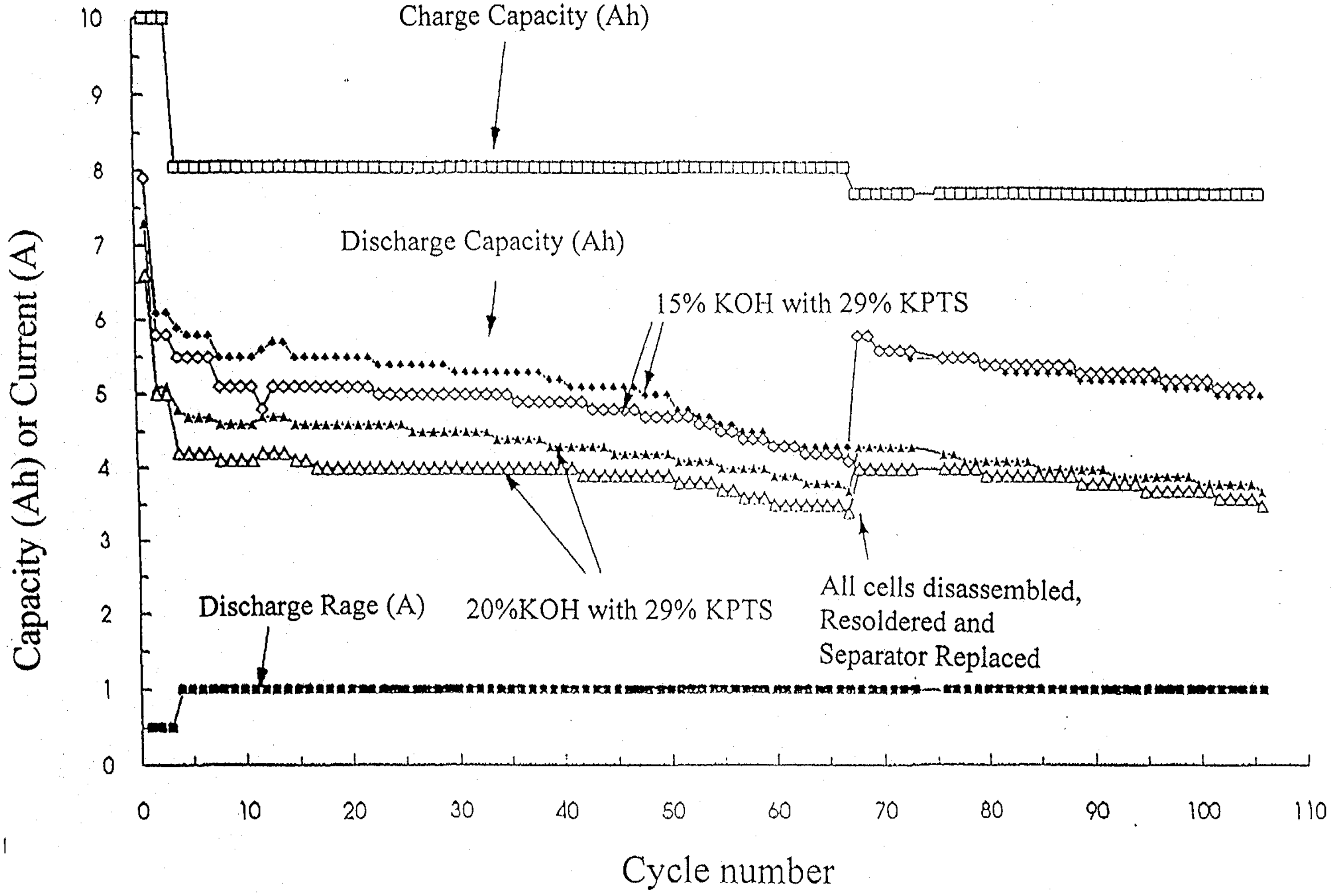

Figure 4. Performance of Zn/NiOOH cells with Westinghouse paste zinc electrodes in KOH solutions containing potassium 1,3,5-phenyltrisulphonate additive.

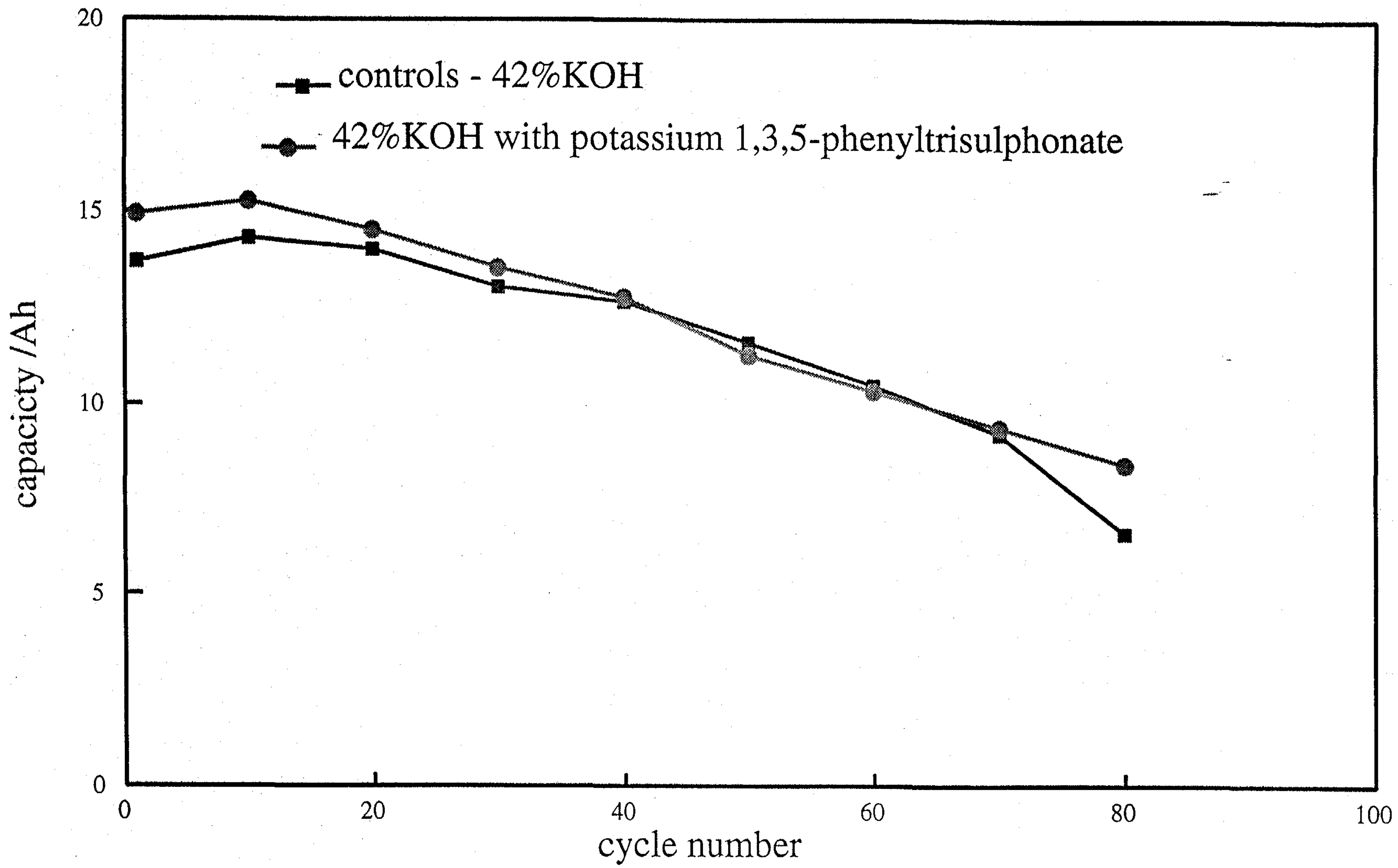

Figure 5. Performance of Zn/AgO Cells