

RECHARGEABLE Li/TiS₂ AA CELLS

A.C. Makrides, K.M. Abraham, G.L. Holleck, T.H. Nguyen, and R.J. Hurd

EIC Laboratories, Inc.
111 Downey Street
Norwood, Massachusetts 02062

Abstract

Performance characteristics of AA cells based on the Li/TiS₂ couple and utilizing a proprietary electrolyte are presented and discussed. These general purpose, medium power, AA cells provide 1.0 Ah, have an average discharge voltage of 2.1v at 23°C, and a service life of 250 full depth of discharge cycles. Their energy density at the C/3 rate is 130 Wh/kg and they can be discharged up to about the C rate without significant loss of capacity. Operating temperatures extend from -20°C to 45°C. Their safety is not compromised by electrical abuse provided cell temperatures do not exceed 140°C.

INTRODUCTION

Lithium/transition metal chalcogenide cells were first described by Whittingham [1]. In particular, he showed that the Li/TiS₂ couple has high energy density, is reversible, and can provide power densities of practical utility.

Early versions of Li/TiS₂ cells used LiClO₄ dissolved in dioxolane as the electrolyte. This electrolyte proved to be unstable; LiAsF₆ has since replaced LiClO₄ as the salt of choice in organic solvents.

The Li/TiS₂ cell as originally reduced to practice was highly promising but had a number of shortcomings. Its cycle life, which is determined by the efficiency of plating lithium, was short. All organic electrolytes react with Li, more or less, to form surface films which largely determine the kinetics and efficiency of plating [2]. An early observation at EIC Laboratories was a high efficiency of plating Li from electrolyte solutions based on 2-methyltetrahydrofuran [3]. This was followed by the important, practical discovery that certain additives, particularly 2-methylfuran, improved dramatically the plating efficiency of Li [4]. Based on these observations, a mixed solvent was developed which has high efficiency over a wide temperature range (-30° to 70°C) [5].

Li/TiS₂ cells are expected to have a negligible rate of self-discharge at any reasonable (<70°C) storage temperature. This expectation is borne out by cells constructed from high purity materials under rigorous conditions, e.g., in a controlled atmosphere "dry" box. However, cells built in a dry (<2% RH) room have appreciable self-discharge, at least early in their cycle life.

Self-discharge is caused by elemental sulfur probably produced during processing of TiS₂ into electrodes [6]. During discharge, sulfur is reduced at the cathode to soluble polysulfides and these diffuse to the Li electrode where they are reduced further. The reduction products diffuse in turn to the cathode where they are oxidized. This polysulfide shuttle eventually lowers the TiS₂ potential to a value corresponding to about 30% discharge of the cell. In the absence of mitigating measures, sulfides are eventually removed during cycling as Li₂S and the self-discharge rate becomes negligible after about 30 to 40 cycles.

A solution to the problem of self-discharge in early cycles has been worked out based on additions to the cathode of small quantities (~0.5% by wt) of sulfur "scavengers", e.g., Al, Cu,

Ni, and Mo among others [7]. Quantitative suppression of self-discharge is achieved without adverse effects on either cycle life or rate capability of the cell [7].

Past work with the Li/TiS₂ couple at EIC Laboratories was primarily carried out with prismatic cells utilizing relatively thick cathodes [8]. The main advantage of prismatic cells is the high energy density achieved when they are assembled into (prismatic) batteries. However, besides their higher cost, prismatic cells suffer from certain disadvantages, particularly from dimensional instability during cycling caused by expansion of the cell stack. The pressure exerted by an expanding stack flexes the large faces of a prismatic cell outwards. The consequent relative movement of stack components affects cycle life adversely. Stack deformation may also lead to an internal short which, of course, terminates the useful life of the cell abruptly. This last problem occurs frequently enough to compromise the reliability of prismatic cells.

Spirally wound, cylindrical cells are free from these shortcomings. We present here performance characteristics of a general purpose, AA cell utilizing a proprietary electrolyte developed by us [4]. This is a medium power cell designed for about 250 cycles of 8 hr discharge followed by overnight charge.

CELL COMPONENTS

Cathodes

The intrinsic properties of TiS₂ are excellently suited to the manufacture of high performance cathodes. TiS₂ has good electronic conductivity in the charged as well as the discharged states, a low equivalent weight, an attractive volumetric energy density, a high mobility for lithium in its crystal lattice, and good temperature stability. The material itself can be produced inexpensively. The technical problem is the production, from powder, of continuous cathodes with good mechanical properties and with uniform thickness and porosity.

Double sided cathodes are produced by pressing a mixture of TiS₂ powder and binders on Al foil approximately 0.02mm thick. Total binder is kept to less than 3 wt% to yield cathodes with an active mass of about 97 wt% TiS₂. Cathode porosity is approximately 30% corresponding to an apparent density of TiS₂ of about 2.2 g/cm³. The overall cathode thickness can be varied from about 0.125 to 0.25mm while uniform (± 5%) loading is maintained. Cathodes thinner than 0.125mm yield cells with too low an energy density; cathodes thicker than about 0.25mm are too stiff to be readily wound.

The initial capacity of Li/TiS₂ cells is fixed by the cathode since Li is in excess over the stoichiometric amount required to discharge the cell. Typically, there is a loss of about 5% of cell capacity in the first few (~5) cycles, apparently due to changes of the cathode. The magnitude of the loss appears to depend on the characteristics of the starting TiS₂ material, the nature of the binder, and the cathode forming conditions. To take account of this loss and of variations in cathode capacity from the mean, cells are rated in terms of a nominal capacity set at 90% of theoretical.

As is well known, lithiation of TiS_2 expands its volume by about 10% [9]. However, the overall volume of a Li/ TiS_2 electrode stack or roll decreases upon discharge since Li atoms pack more tightly in TiS_2 than in Li metal. This decrease is more than offset, as a cell is cycled, by "growth" of the Li electrode, probably caused by changes in the morphology of plated Li.

The Anode

Lithium foil is used as the anode. The foil is unsupported, that is, a current collector is not used. The thickness of the Li foil is selected to provide the desired excess of Li over the stoichiometric requirement. In practice, there is a lower limit of about 0.125mm set by cost and by handling requirements during winding.

A practical problem of some significance is the electrical contact to the relatively soft, unsupported Li foil. Spot welding of a properly designed mechanical connection gives a reliable, low resistance contact whose integrity is maintained throughout the life of the cell.

The Electrolyte

The electrolyte is a 1.5M solution of $LiAsF_6$ in an approximately equimolar mixture of tetrahydrofuran and 2-methyltetrahydrofuran with 3 vol% of 2-methylfuran. Its density at 20°C is 1.1170 g/cm³ and its conductivity ranges from 3.0×10^{-3} at -40°C to 11.0×10^{-3} (ohm cm)⁻¹ at 60°C. Its viscosity at 20°C is 2.845 cp. The diffusion coefficient of the salt is approximately 5×10^{-6} cm²/sec at 20°C.

Other Cell Components

A single layer, 0.025mm thick, of microporous polypropylene (Celgard 2400, Hoechst Celanese) is used as a separator between anode and cathode.

The can and cover are 304 stainless steel. The Li is connected to the can and the positive electrode contact is isolated with a glass-to-metal seal (Corning 9013). The cell is filled through the cover and is hermetically sealed by welding.

The total weight of an AA cell is approximately 16g. It is of interest to note that Li contributes only about 7% of the weight. Cell hardware accounts for about 40%, the cathode for about 35%, and the electrolyte for 17% of the total weight.

CELL DESIGN

Energy Density, Power, and Cycle Life

The energy density is a direct function of cathode thickness for a fixed amount of Li. The energy density also depends on the discharge rate which, in turn, largely defines the power delivered by the cell. Cycle life depends on the ratio of Li to the stoichiometric requirement. Energy density and cycle life are related through the Li ratio. This is an inverse relation, that is, energy density decreases while cycle life increases as the Li ratio is raised.

The relation between nominal capacity and cathode thickness is shown in Figure 1 for cathodes of fixed porosity (30%). The total variation of capacity over the practically useful range of cathode thickness is somewhat less than 20%. The relatively low sensitivity of nominal capacity to cathode thickness at a fixed Li ratio is a result of the low density of Li.

The rate capability, and hence the power density, of a cell depends on the kinetics, including mass transport, at the cathode.

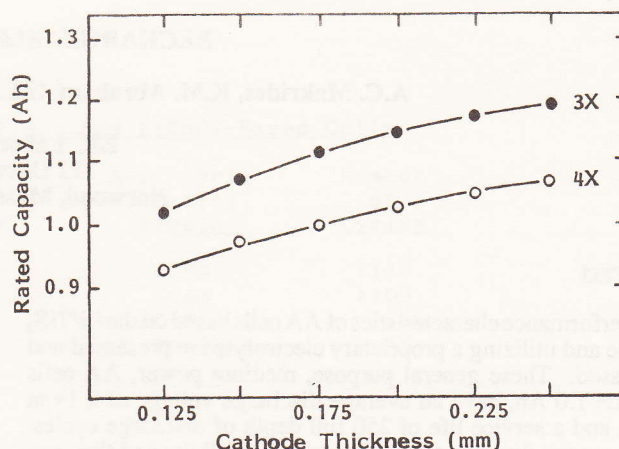


Fig. 1. Capacity of AA cells at the C/3 rate as a function of cathode thickness for two Li to stoichiometric ratios.

However, differences in kinetics for cathode thicknesses within the range relevant here are relatively small. Figure 2 shows that the realizable capacity is essentially the same for 0.15 and 0.22mm thick cathodes at all current densities up to 10 mA/cm². Thus, the main effect of cathode thickness on power density arises through its influence on the total electrode area of the cell.

The relation between energy density and power density is shown in Figure 3 for two cathode thicknesses at a fixed Li to stoichiometric ratio of 4.0. The crossover point for higher power cells, in this instance approximately 400 W/L (about the 1.5C rate), depends on the Li ratio. For example, if this ratio is 3.0, the crossover point is 500 W/L.

The relation of cycle life to the Li ratio should be linear, if the efficiency of plating Li is constant. The number of cycles delivered by a cell is given by

$$\text{cycles} = (R_{Li} - R_o) a_{th} / (1 - \text{efficiency}) a_{av}$$

where R_{Li} is the ratio of Li to the stoichiometric requirement, R_o is the ratio of available Li at the "end-of-life" (typically 0.7) to stoichiometric capacity, a_{th} is the capacity per unit area for a full (theoretical) cycle and a_{av} is the average capacity per unit area per cycle actually delivered over the life of the cell. Since the cumulative capacity delivered by the cell is equal to $a_{av} \times$ (number of cycles), we can also write

$$\text{cumulative capacity/cm}^2 = (R_{Li} - R_o) a_{th} / (1 - \text{efficiency})$$

The efficiency of plating Li is determined in the first instance by the composition (and properties) of the electrolyte. However, it also depends on other variables including details of construction of the electrode stack. Leaving these aside for the present, the other main variable which influences efficiency is the charge density (mAh/cm²) of the cycle. For full discharge cycles, this last quantity is directly proportional to cathode thickness.

The dependence of (1-efficiency) on cycle charge density is shown in Figure 4. The efficiency increases from about 99.0% at 4 mAh/cm² to 99.5% at 2 mAh/cm². Although the magnitude of the increase may not appear to be large, its effect on cycle life is substantial, in this case the cycle life doubles.

It turns out, therefore, that the relation between energy density, power density, and cycle life is complex even within the parameter envelope relevant to practically useful cells. The cell characteristics depend on several interconnected variables among which cathode thickness is particularly significant.

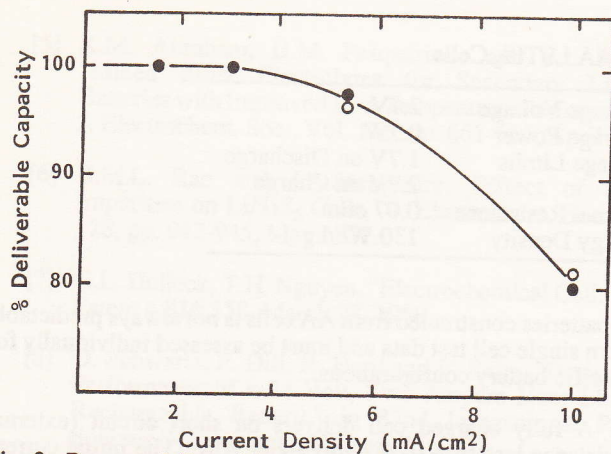


Fig. 2. Percent deliverable capacity as a function of current density for 0.147mm (o) and 0.22mm (●) thick cathodes at cycle 20 and 23°C.

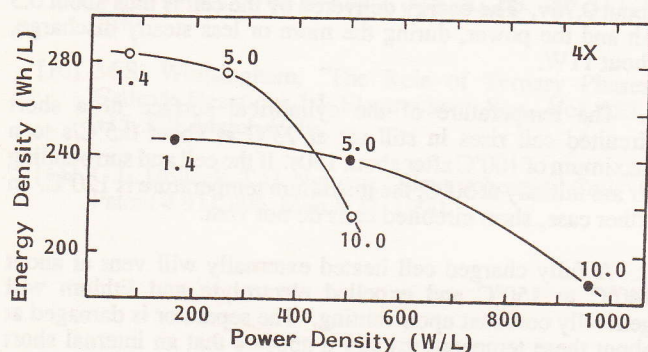


Fig. 3. Energy density as a function of power density at 4X Li at 1.4, 5.0 and 10 mA/cm² at 23°C for cathodes 0.125 (●) and 0.25 (o) mm thick.

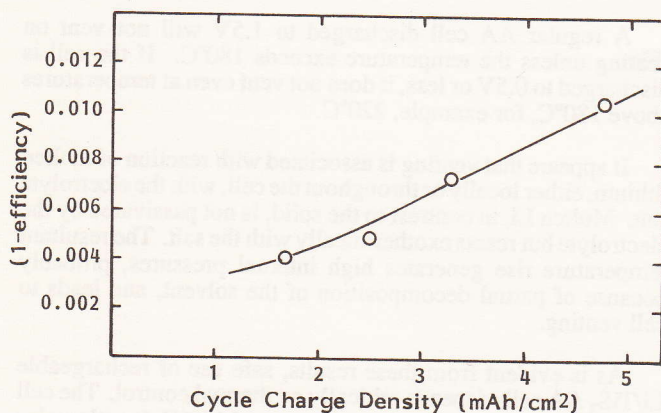


Fig. 4. The dependence of Li efficiency on cycle charge density at 23°C.

CELL PERFORMANCE

General Purpose Cells

Many industrial and military applications of rechargeable power sources require eight hours of operation followed by overnight recharge. The cycle life of the battery should be sufficient for at least one year of service, and preferably longer since battery replacement is a significant operating cost, though frequently not the main one. A battery based on Li/TiS₂ AA cells is suitable for many of these applications and provides power at energy densities which compare favorably with currently available alternatives, for example, lead acid or

nickel-cadmium batteries. Performance characteristics of a general purpose, Li/TiS₂ cell are given in Table 1 and elaborated upon below.

Capacity. The cell utilizes a 0.21mm thick cathode with 30% porosity to yield a theoretical capacity of 1.15 Ah and a nominal capacity of 1.0 Ah. The capacity rating is at a current density of 1.4 mA/cm² or 0.35A (approximately the C/3 rate). The dependence of capacity at 23°C on discharge rate is shown in Figure 5. Approximately 70% of the capacity is available at 2A (2C rate).

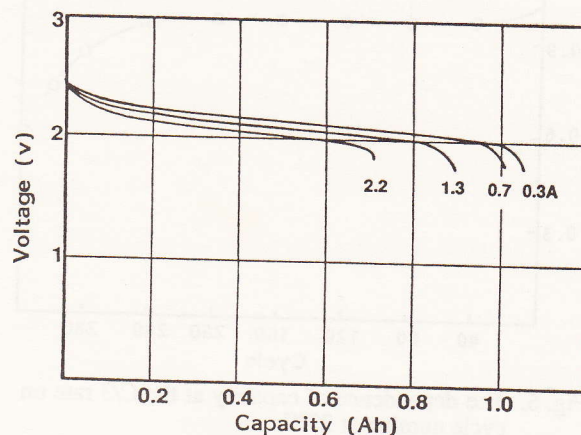


Fig. 5. Voltage as a function of delivered capacity at various discharge rates for AA cells at 23°C.

Power. The average power delivered by the cell is the product of the discharge rate and the average cell voltage. As is well known [10], the reversible potential of Li_xTiS₂ decreases as Li is incorporated into the lattice. At mid-discharge (x ~0.5) the potential is 2.20V vs. Li/Li⁺; it decreases to 1.9V for full discharge (x ~1).

The mid-point voltage during discharge of an AA cell at the C/3 rate is 2.15V. The average voltage during discharge is slightly less. Ohmic losses (internal resistance ~0.07 ohm) account for about 0.02V of the decrease from the reversible value and other polarization losses for the rest. Thus, the average power delivered during discharge at the C/3 rate is 0.7W (about 85 W/L). The range of useful power densities extends to about 500 W/L.

Cycle Life. The cycle life is defined by the number of standard cycles delivered before the capacity declines below 80% of nominal. A standard cycle consists of discharge at 0.35A to a cutoff voltage of 1.7V and charge at 0.17A to 2.7V at 23°C. A standard cycle for this cell corresponds approximately to 4 mAh/cm².

The cycle life of the AA cell is 250 cycles. Since the cell has a Li ratio of 3.2 (3.5 on the basis of nominal capacity), the average efficiency of plating Li over its cycle life is approximately 99.0%.

The capacity delivered by a standard cycle is shown as a function of cycle number in Figure 6. The capacity is nearly constant at 95% or more of nominal during most of the cell life but declines rapidly, within 25 cycles, to the cutoff limit (80% of nominal) near the end of life. There is, however, a gradual loss of power capability, accompanied by a rise in internal resistance, as the cell is cycled. This is probably a result of deterioration in mass transport conditions at the Li electrode caused by an increasingly unfavorable morphology of plated Li.

Table 1. Performance of AA Li/TiS₂ Cells

Nominal Capacity	1.0A	Average Voltage	2.1V
Nominal Discharge Rate	0.35A	Average Power	0.7W
Nominal Charge Rate	0.17A	Voltage Limits	1.7V on Discharge
Cycle Life (at 23°C)	250 cycles		2.7V on Charge
Operating Temperature	-20° to 45°C	Internal Resistance	0.07 ohm
Weight	16 g	Energy Density	130 Wh/kg

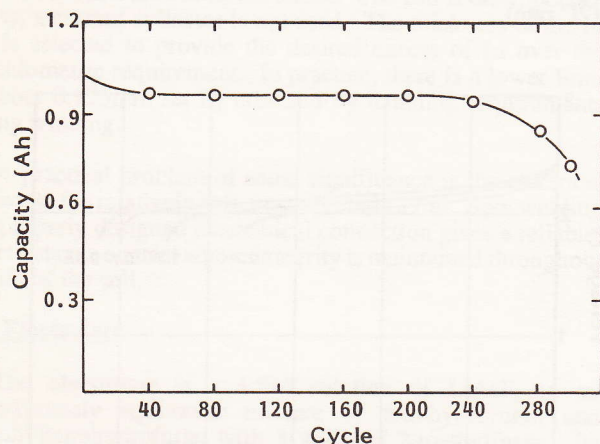


Fig. 6. The dependence of capacity at the C/3 rate on cycle number at 23°C.

Cycle life is relatively insensitive to the discharge rate, at least below 1A. Cycle life depends, however, on the charge rate. The maximum permissible charge rate is 0.25A (C/4); higher charge rates reduce the cycle life significantly.

Voltage Limits. The voltage limits, 1.7V on discharge and 2.7V on charge, can be relaxed somewhat without compromising cycle life. The discharge limit can be lowered to 1.6 or 1.5V without damage to the cell. However, discharge below 1.5V for a prolonged period leads to an irreversible loss of capacity and of rate capability caused by electrolyte (salt) reduction at the cathode.

The charge limit can be extended to 3.1V without a significant effect on cycle life. For example, cells charged at C/6 to 2.7V and then at C/40 (~25 mA) to 3.1V perform as well as cells subjected to a standard cycle.

Operating Temperature. The capacity delivered at C/3 at -20°C, the lower limit of operating temperatures, is 80% of that at room temperature. Some capacity (~50%) can be delivered at -30°C.

The high temperature operating limit of 45°C is set by electrolyte reduction, particularly at low voltages (1.5 to 1.6V). Electrolyte side reactions can be suppressed by suitable surface coatings on the cathode without apparently affecting the rate capability of the cell [11]. However, this requires additional processing of the TiS₂ which was not carried out for these prototype cells.

Safety. Safety is an obvious concern since rechargeable, in contrast to primary, Li cells have an excess of Li over the stoichiometric requirement. Furthermore, the Li electrode increases in surface area and hence in potential reactivity as a rechargeable cell is cycled. On the other hand, organic electrolytes are generally less aggressive than electrolytes commonly used in primary cells.

The response of Li/TiS₂ AA cells to electrical and thermal abuse was assessed from tests with single cells. The response

of batteries constructed from AA cells is not always predictable from single cell test data and must be assessed individually for specific battery configurations.

A fully charged cell delivers on short circuit (external resistance less than 0.07 ohm) about 20A. The initial current pulse declines rapidly (~5s) to a more or less steady current of about 15A which lasts for about 120s before it declines, again rapidly, to negligible values. Cell voltage at the 15A plateau is about 0.75v. The energy delivered by the cell is thus about 0.5 Ah and the power, during the more or less steady discharge, about 11W.

The temperature of the cylindrical surface of a short circuited cell rises in still air at 23°C at about 0.5°C/s to a maximum of 100°C after about 150s. If the cell and surrounding air are initially at 50°C, the maximum temperature is 120°C. In either case, short circuited cells do not vent.

A fully charged cell heated externally will vent at about 140°C to 150°C and expelled electrolyte and lithium will generally combust upon venting. The separator is damaged at about these temperatures and it appears that an internal short develops when the separator loses its integrity. If a separator stable to at least 200°C is substituted for microporous polypropylene, a fully charged cell will not vent unless its temperature rises above 180°C, the melting point of Li.

A regular AA cell discharged to 1.5V will not vent on heating unless the temperature exceeds 180°C. If the cell is discharged to 0.5V or less, it does not vent even at temperatures above 180°C, for example, 220°C.

It appears that venting is associated with reaction of molten lithium, either locally or throughout the cell, with the electrolyte salt. Molten Li, in contrast to the solid, is not passivated by the electrolyte but reacts exothermically with the salt. The resultant temperature rise generates high internal pressures, probably because of partial decomposition of the solvent, and leads to cell venting.

As is evident from these results, safe use of rechargeable Li/TiS₂ AA cells depends critically on thermal control. The cell temperature must not be allowed to exceed 140°C, for otherwise the cell may vent and the expelled materials will combust in air.

REFERENCES

- [1] M.S. Whittingham, "Chalcogenide Battery," U.S. Patent 4,009,052, February 22, 1977.
- [2] D. Aurbach, M.L. Daroux, P.W. Faguy and E. Yeager, "Identification of Surface Films formed on Lithium in Dimethoxyethane and Tetrahydrofuran Solutions," *J. Electrochem. Soc.*, Vol. 135, pp. 1863-1871, Aug. 1988.
- [3] V.R. Koch, "Aprotic Solvent Electrolytes and Batteries Using Same," U.S. Patent 4,118,550, Oct. 3, 1978.
- [4] K.M. Abraham, S.B. Brummer, J.S. Foos, "Lithium Battery," U.S. Patent 4,489,145, Dec. 18, 1984.

- [5] K.M. Abraham, D.M. Pasquariello and F.J. Martin, "Mixed Ether Electrolytes for Secondary Lithium Batteries with Improved Low Temperature Performance," J. Electrochem. Soc., Vol. 133, pp. 661-666, April 1986.
- [6] B.M.L. Rao and J.A. Shropshire, "Effect of Sulfur Impurities on Li/TiS₂ Cells," J. Electrochem. Soc., Vol. 128, pp. 942-945, May 1981.
- [7] G.L. Holleck, T.H. Nguyen, "Electrochemical Cell," U.S. Patent 4,816,358, March 28, 1989.
- [8] D. Schwartz, P. Hill, R. Hurd and P. Rebe, "Design and Performance of a 24 Volt, Two Ampere Hour Lithium Rechargeable Battery," in 32nd International Power Sources Symposium, 1986, pp. 226-232.
- [9] J.R. Dahn, M.A. Py and R.R. Haering, "In Situ X-Ray Diffraction Experiments on Lithium Intercalation Compounds," Can. J. Phys., Vol. 60, pp. 307-313, Feb. 1982.
- [10] M.S. Whittingham, "The Role of Ternary Phases in Cathode Reactions," J. Electrochem. Soc., Vol. 123, pp. 315-320, March 1976.
- [11] G.L. Holleck, T.H. Nguyen, "Electrochemical Cell," U.S. Patent 4,911,996, March 27, 1990.