

A lithium-ion cell with an inorganic electrolyte

Arden P. Johnson*, Carl R. Schlaikjer

Battery Engineering, Inc., 1636 Hyde Park Avenue, Hyde Park, MA 02136, USA

Accepted 2 December 1996

Abstract

A novel rechargeable cell is described in which a carbon-based negative electrode operates in an inorganic electrolyte containing sulfur dioxide. The discharge reaction involves the reduction of sulfur dioxide at a positive electrode composed of carbon. Both the negative and the positive electrodes thus consist of carbon, the former of graphite or a low surface area carbon, and the latter of a high surface area carbon. Lithium ions are introduced into the carbon electrodes from a sacrificial lithium electrode. This system combines the safety advantages of a non-metallic negative electrode with the excellent reversibility of the sulfur dioxide depolarizer. Because no metal oxide cathode is used, only abundant and inexpensive materials are required. © 1997 Published by Elsevier Science S.A.

Keywords: Rechargeable lithium batteries; Sulfur dioxide; Lithium-ion batteries; Inorganic electrolytes

1. Introduction

The lithium/SO₂ rechargeable system is highly advantageous in that it shows long shelf life, high energy density, and resistance to overcharging, and the cells require only inexpensive and readily available materials [1]. The sulfur dioxide electrolyte in this system acts as the depolarizer, and during discharge is reduced at a cathode composed of carbon. Because of safety problems which can arise due to dendrite formation during charging, however, cells of this type have found no practical use.

By contrast, organic lithium-ion cells with carbon negative electrodes and metal oxide positive electrodes show excellent safety characteristics, though they must be carefully protected against overcharging [2]. The stable cycling of carbon negative electrodes in a sulfur dioxide electrolyte has been reported [3], and the reversible cycling of lithiated metal oxide cathodes in sulfur dioxide electrolytes has also been described [4]. In a cell containing such a metal oxide cathode, the sulfur dioxide would act as a liquid electrolyte, but would not be expected to be involved in the reduction reaction at the cathode.

We report here a novel rechargeable cell in which a carbon-based negative electrode operates in an inorganic electrolyte

containing sulfur dioxide. No metal oxide is present, and the cell discharge reaction involves the reduction of the sulfur dioxide depolarizer at a carbon cathode. Remarkably, then, both the negative and the positive electrodes consist of carbon, the former of graphite or a low surface area carbon, and the latter of a high surface area carbon. Lithium ions are introduced into the carbon electrodes from a sacrificial electrode of lithium metal.

2. Experimental

Negative electrodes were constructed by pressing a mixture of a lithium-intercalating carbon with 3 wt.% of poly-(tetrafluoroethylene) (PTFE) binder onto a current collector of nickel expanded metal screen. Positive electrodes were constructed similarly using a 3:1 mixture by weight of acetylene black (Chevron) and Ketjen black (AKZO) and 10 wt.% PTFE pressed onto a current collector of aluminum expanded metal screen. A sandwich of these electrodes and a sacrificial electrode of lithium metal was wound in a spiral configuration and inserted into a 14 mm × 48 mm stainless-steel can. The carbon electrodes were electrically connected to separate contact pins, which were isolated by glass-to-metal seals. The lithium metal electrode was electrically connected to the cell case.

* Corresponding author. Tel.: (617) 361-7555; Fax: (617) 361-1835

An electrolyte of composition $2\text{LiCl} \cdot \text{CaCl}_2 \cdot 4\text{AlCl}_3 \cdot 12\text{SO}_2$ was prepared by refluxing the appropriate stoichiometric quantities of LiCl , CaCl_2 and AlCl_3 in distilled SO_2Cl_2 for 6 h and then boiling off the sulfuryl chloride [5,6]. Sulfur dioxide gas was allowed to flow over this dried salt mixture until no more SO_2 was absorbed. A clear solution was obtained. The cells were filled with 3.0 ml of the electrolyte through a fill tube which was then sealed by crimping.

The lithium was discharged against each of the carbon electrodes, to a cut-off of 2.0 V for the positive electrode, and either 0.5 or 0.1 V for the negative electrode. The sacrificial lithium electrode was then disconnected, and the cells were cycled between the carbon electrodes at a constant current density of 0.7 or 1.4 mA/cm^2 between potential limits of 4.0 and 1.0 V. Computer-controlled power supplies with automated data collection (Starbuck and Maccor) were used for the charge and discharge cycling.

3. Results and discussion

An example of the discharge of lithium metal versus a positive electrode composed of a mixture of acetylene black and Ketjen black is shown in Fig. 1. The processes in this cell discharge reaction take place at cell potentials between 3.4 and 2.7 V, and consist of reduction of the sulfur dioxide at the carbon surface to form a species in which a reduced complex of sulfur dioxide and aluminum chloride is bound to the surface of the carbon [7]. Because the reduction involves the surface of the carbon, it is advantageous to use carbons in the cathode which have a high specific surface area; Ketjen black, for example, has a specific surface area of about $950 \text{ m}^2/\text{g}$.

A similar curve is shown in Fig. 2 for the discharge of lithium metal versus an electrode composed of Lonza KS-15 graphite. A brief period of discharge takes place as above at potentials higher than 2 V. Additional processes, however, occur at potentials below 2 V. These latter processes evidently involve intercalation of lithium ions into the graphite structure. It is this intercalation which allows a carbon negative electrode to act as the negative electrode in a cell in which a carbon negative electrode is cycled versus a carbon positive electrode. In order to minimize the amount of lithium which is spent in the discharge processes that take place above 2 V, it is advantageous in the negative electrode to use carbons which have a relatively low specific surface area; Lonza KS-15 graphite, for example, has a specific surface area of about $12 \text{ m}^2/\text{g}$.

Fig. 3 shows typical charge and discharge curves for a cell in which a Lonza KS-15 graphite negative electrode was cycled versus an acetylene black/Ketjen black positive electrode. Cycles 57 to 59 are depicted. The capacity as a function of cycle number for the same cell is shown in Fig. 4 for the first 250 cycles. The performance of various types of carbon was compared in tests of this sort, including the graphites Lonza KS-15 and Lonza SFG-6, and a coke, Mitsubishi MBC-N. In these tests, the graphite electrodes delivered much greater cycle life than did the electrodes containing coke. Fig. 5 shows cycle performance for one cell in which the negative electrode was composed of Mitsubishi MBC-N coke.

It is very interesting to observe in Fig. 4 that the discharge capacity continued to increase for over 100 cycles before reaching a maximum. Excess lithium metal remained in the cell after the initial steps in which the lithium was discharged against the carbon electrodes. It is evident from the increasing discharge capacity that this lithium metal continued to be

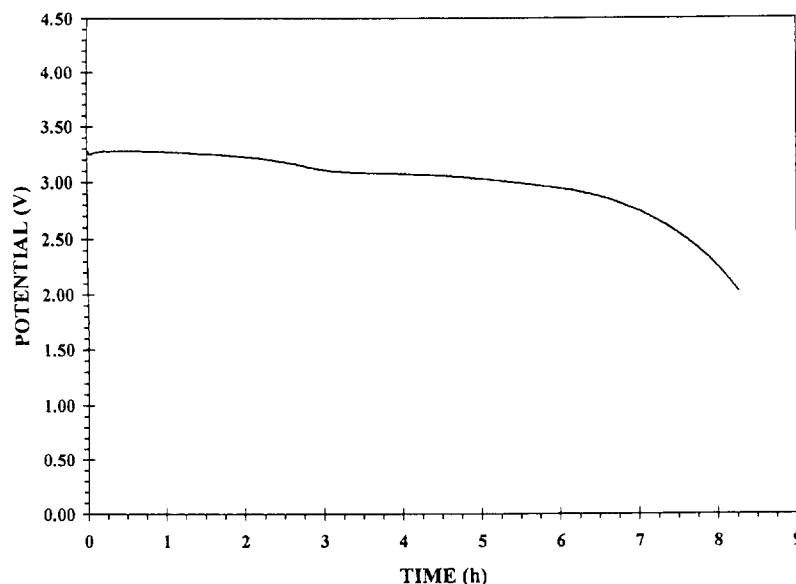


Fig. 1. Discharge of sacrificial lithium electrode vs. carbon electrode composed of acetylene black and Ketjen black (3:1); current density: $1.4 \text{ mA}/\text{cm}^2$

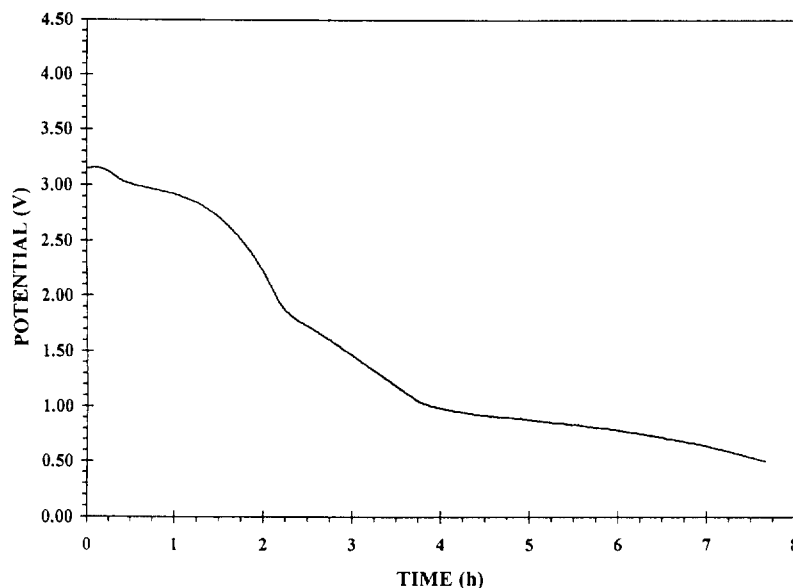


Fig. 2. Discharge of sacrificial lithium electrode vs. carbon electrode composed of Lonza KS-15 graphite. current density: 1.4 mA/cm²

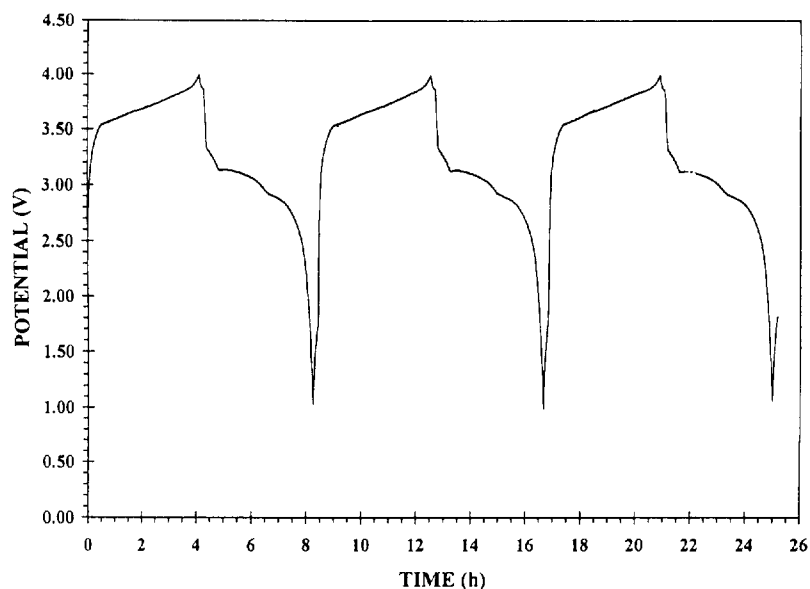


Fig. 3. Charge and discharge for cycle nos 57 to 59 in a cell containing a negative electrode composed of Lonza KS-15 graphite; current density 1.4 mA/cm².

transferred into the active electrodes during the cell cycling even though it was electrically disconnected before cycling between the carbon electrodes was started. In some cells the discharge capacity continued to increase for several hundred cycles.

In cells which were charged with an upper voltage limit set at 4.1 V, the potential would rise during charging to about 4.05 V, where it would remain steady indefinitely, consuming charge to many times the discharge capacity of the cell. After such overcharging, cells treated in this manner delivered the

normal discharge capacity, and their subsequent performance was otherwise unaltered. This behavior demonstrates the existence of an overcharge protection mechanism in this cell system which is presumably the same as that which has been observed in sulfur dioxide secondary cells with lithium metal anodes. This mechanism has been understood to involve oxidation of AlCl_4^- at the positive electrode during overcharging to give Cl_2 and AlCl_3 . The Cl_2 is reduced at the negative electrode to give chloride ion, which reacts with AlCl_3 to restore the AlCl_4^- [7]. More recent evidence suggests that

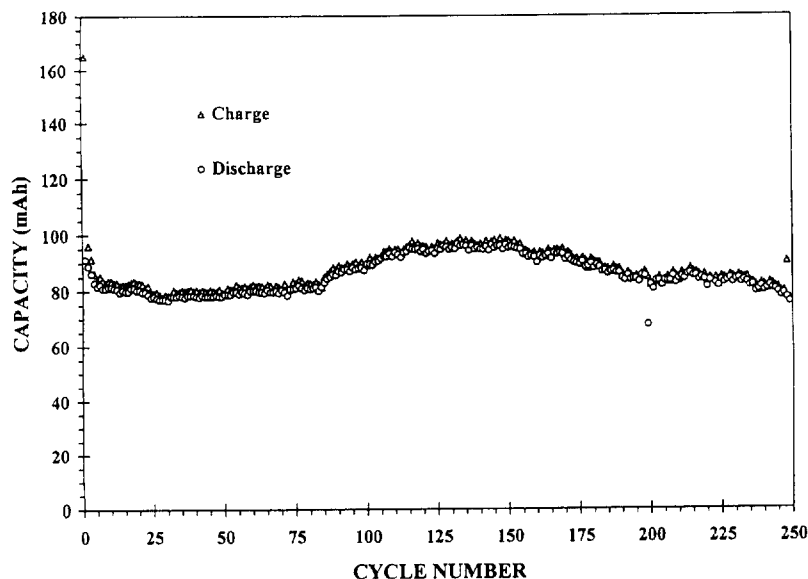


Fig. 4. Capacity as a function of cycle number for a cell containing a negative electrode composed of Lonza KS-15 graphite; current density: 1.4 mA/cm²

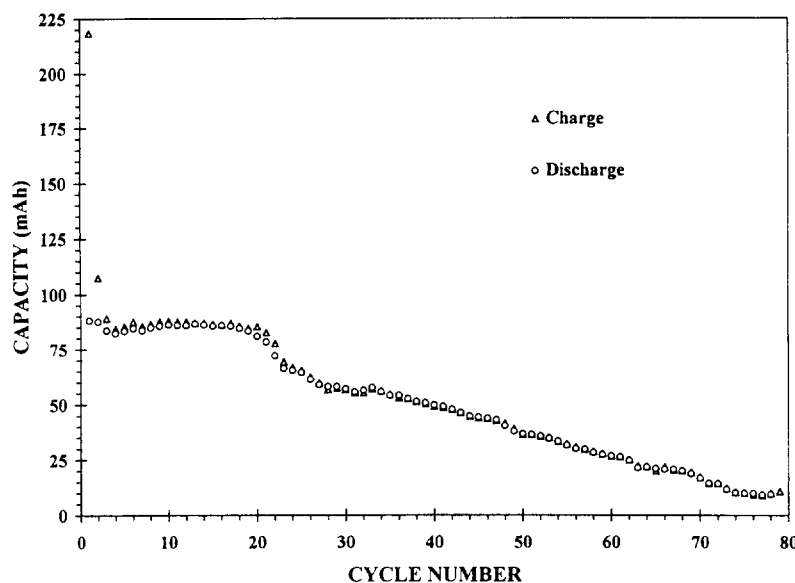


Fig. 5. Capacity as a function of cycle number for a cell containing a negative electrode composed of Mitsubishi MBC-N coke; current density: 0.7 mA/cm².

the Cl₂ reacts with the SO₂ to produce SO₂Cl₂, and it is this latter species that is reduced at the negative electrode [8]. In either case, the overcharging produces no net reaction.

4. Conclusions

In this work, we have demonstrated the successful cycling of a carbon-based negative electrode in a rechargeable cell with a sulfur dioxide electrolyte. Whereas rechargeable SO₂ cells with lithium metal anodes can explode with great violence during cycling due to shorting of lithium dendrites to the positive electrode, we have observed no such hazardous behavior in extensive testing of cells where carbon negative

electrodes are used. In providing safety against dendrite formation, this inorganic lithium-ion system combines the advantages of a non-metallic negative electrode with the excellent reversibility and protection against overcharging which the sulfur dioxide depolarizer offers [9].

Acknowledgements

Samples of Lonza KS-15 and Lonza SFG-6 were generously provided by Timus Corporation, Westlake, OH, USA. Samples of MBC-N were generously provided by Mitsubishi Chemical Corporation, Tokyo, Japan.

References

- [1] H.C. Kuo, D.L. Foster, C.R. Schlaikjer, M.L. Gopikanth and A.N. Dey, *US Patent No. 4 513 067* (1985).
- [2] T. Nagaura and K. Tozawa, *Prog. Batteries Solar Cells*, 9 (1990) 209–217.
- [3] J.O. Besenhard, M. Winter, J. Yang and W. Biberacher, *J. Power Sources*, 54 (1995) 228–231.
- [4] J. Dreher, B. Haas and G. Hambitzer, *J. Power Sources*, 43–44 (1993) 583–587.
- [5] C.R. Schlaikjer, *US Patent No. 4 925 753* (1990); *Re. 33 995* (1992).
- [6] C.R. Schlaikjer, *US Patent No. 5 145 755* (1992)
- [7] A.N. Dey, H.C. Kuo, P. Piliero and M. Kallianidis, *J. Electrochem Soc.*, 135 (1988) 2115–2120.
- [8] M. Golezinowski, R.J. Doré and I.R. Hill, *J. Power Sources*, 54 (1995) 356–361.
- [9] A.P. Johnson and C.R. Schlaikjer, *US Patent Applic., Ser. No. 08/601 980*