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Measurement of Lithium Cycling Efficiency in Organic Electrolytes

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May 1991

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13. ABSTRACT (Maximum 200 words) An experiment to measure the average lithium cycling efficiency of organic electrolytes has been developed. Lithium cycling efficiency is an important parameter in the research and development of rechargeable lithium batteries. The safety, shelf life, and cycle life of lithium batteries are direct consequences of how electrochemically stable the lithium anode is in the organic electrolyte used. Detailed within this report is the method of measurement and its advantages and disadvantages. Also reported are results of lithium cycling efficiencies in various ester solvent-based electrolytes. The effects of cosolvents and electrolyte additives have been investigated.				
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INTRODUCTION

The demand for improved energy storage devices has increased steadily with the emergence of new technologies that require advanced batteries as power sources. In the development of ambient temperature rechargeable lithium batteries, the efficient cycling of the Li negative electrode is essential for long cycle life and storage. One of the major difficulties in the development of high-energy lithium batteries is the strong electrolyte-reducing potential of lithium metal. Lithium is thermodynamically unstable with most organic solvents that are used to prepare electrolytes. However, some solvents (i.e., aprotic) form protective passivating films that provide the electrode surface with some kinetic stability. Other desired properties for an electrolyte used in rechargeable lithium batteries are: high conductivity, high oxidation potential, and a wide usable temperature range.

A simple experiment is described herein, which determines the lithium cycling efficiency in aprotic organic-solvent-based electrolytes. In recent years, many researchers have found the measurement of lithium cycling efficiency a valuable tool in their battery research.¹⁻¹⁰ The effects of solvent purification,¹¹ electrolyte composition, chemical additives,^{12,13} and electrode pretreatments can be determined with this type of experiment.

Knowledge of an electrolyte's cycling efficiency may assist battery engineers in determining the number of cycles a cell can perform, based on the cell capacity and amount of lithium in the cell. Sealed cells have a fixed volume for the amount of active materials: anode, cathode, and electrolyte. When using a poor lithium-cycling electrolyte, an excess lithium-to-cathode ratio must be used to compensate for cycling inefficiencies. This, however, reduces the cells overall rated capacity, which is maximized when the anode-to-cathode ratio is unity. Also, a large amount of lithium in a cell can present safety and disposal problems.

Lithium cycling efficiencies are used for comparisons of the stability of lithium metal in various organic solvent-based electrolytes. The results of cycling experiments indicate whether or not the surface morphology is favorable to repeated lithium plating and stripping cycles. This study details a cycling experiment that can be used to measure the plating efficiency of lithium, as well as other electrode materials in either aqueous or nonaqueous electrolytes. Also reported are some results on lithium cycled in various ester-based electrolytes.

EXPERIMENTAL

The cycling experiment involves a known amount of lithium that is plated electrochemically onto a lithium-working electrode from a lithium counter electrode, and subsequently stripped off. The initial lithium on the working electrode is considered excess. Loss in plating/stripping efficiency will require lithium to be removed from the working electrode to complete the cycle. When the excess lithium is depleted, the experiment is completed. The capacity of the working electrode is less than the counter electrode. The capacity of each plate and strip cycle is less than the initial capacity of the working electrode. This closely represents the situation that would be present in a positive electrode limited lithium secondary cell. Lithium metal should be utilized for both the working and counterelectrode to avoid any possibility of alloy formation or dissolution of other metals, which can occur when nickel, aluminum, or stainless steel is used as counter electrode.

Lithium cycling tests were performed in a wick-type cell configuration, as shown in Fig. 1. The wick cell operates by using a porous glass fiber separator between the electrodes and drawing electrolyte from a small reservoir. This method simulates a real cell environment that would be electrolyte starved. The current collectors were 2.57 cm² nickel disks (Johnson-Matthey 99.997 percent Ni foil) set in a Teflon electrode assembly, as shown in Fig. 2. Lithium disks with a surface area of 2.57 cm² were pressed onto the nickel current collectors. The working electrode utilized 0.124 mm-thick lithium; the counter electrode was made from 0.391 mm-thick lithium. The Teflon holders were fastened together with stainless steel screws that compressed the cell stack assembly and maintained the electrodes parallel to each other, thus ensuring uniform current distribution across the lithium surface. To avoid dendritic shorting, each electrode was sealed in Celguard 2400 polypropylene separator material.

The cell was sealed in a Pyrex glass pressure vessel that was equipped with a Viton rubber O-ring seal. Connections to the cell were performed via nickel wire, vacuum-type feedthroughs affixed at the top of the glass vessel. The wires were insulated with Teflon tubing to prevent shorting. A stainless-steel tee with a 1/8-inch quick connect was used to backfill electrolyte. The backfill method consisted of degassing the cell under a vacuum and drawing the electrolyte through a tube attached to a three-way valve connected to the quick-connect of the cell assembly. This method gave excellent wetting of the electrodes, wick, and separators.

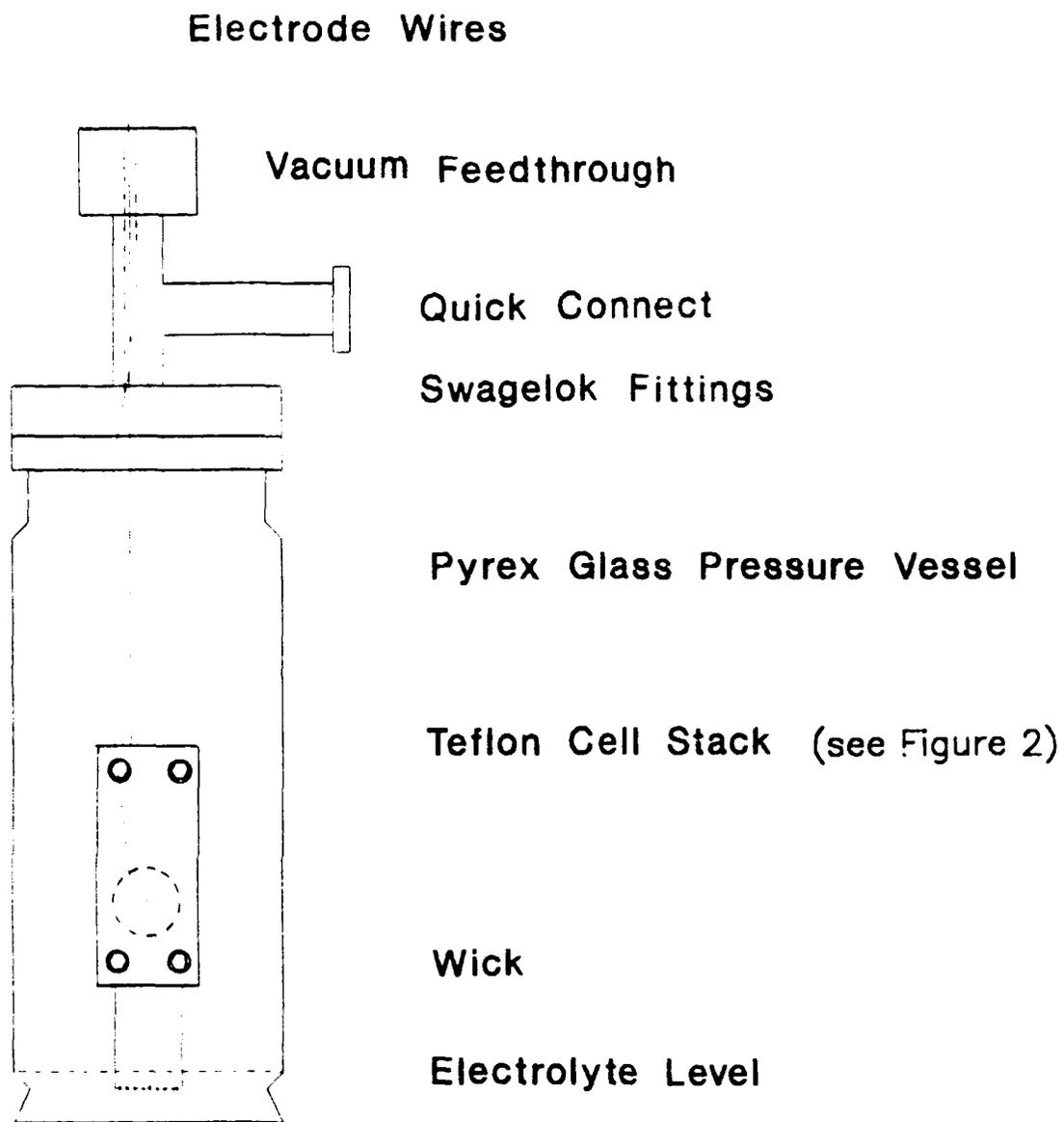


FIGURE 1. Cell assembly of wick-type cell.

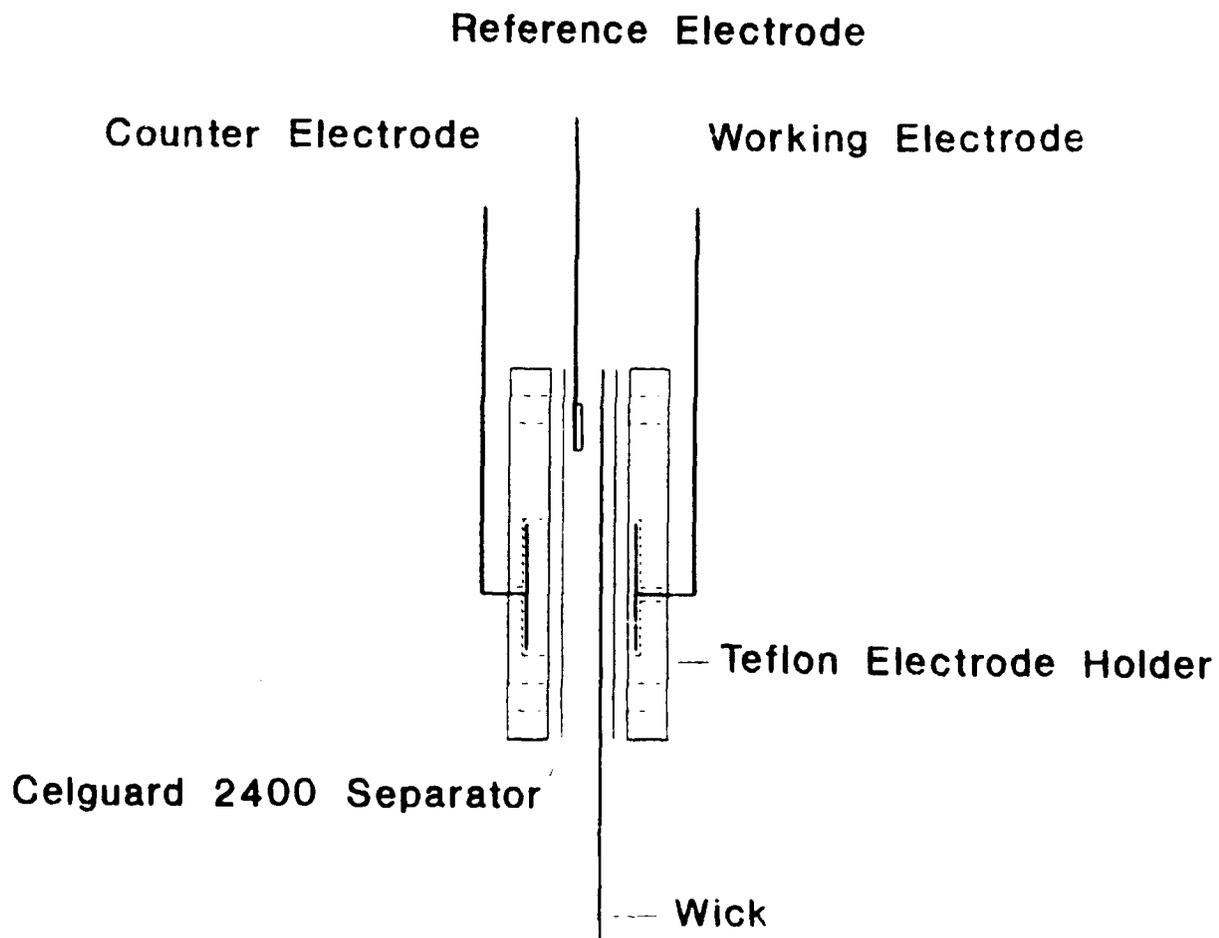


FIGURE 2. CELL STACK ASSEMBLY

Cells were prepared in an argon-filled dry box (less than 1.0 ppm H₂O). Cycling was performed with a PAR Model 273 potentiostat/galvanostat operated in the galvanostat mode. The cells were tested in a Tenney environmental chamber at 25 °C. A three-probe electrometer was used, with a lithium reference located within the cell stack. The galvanostat was controlled with a Hewlett-Packard (HP) basic computer program in conjunction with a HP Series 80 computer. The plating-/stripping-capacity density used was 10 C/cm² (25.7 coulombs). Current densities were 1.0 mA/cm² for both the plating i_p and stripping i_s . The working electrode was preconditioned with an initial strip at 0.1 mA/cm². Cycling was continuous (with no rest periods), and was terminated when the cell polarization versus the lithium reference reached 0.3 volts, which indicated the depletion of lithium from the working electrode.

The solvents, methylformate (MF), diethylcarbonate (DEC), and dimethylcarbonate (DMC) were reagent grade (99+% purity), and were treated with type 4A molecular sieves for 24 hours, followed by fractionation under argon. Karl Fisher titrations of these solvents indicated water contents less than 20 ppm. Ethylene carbonate (EC) was dried over four ampere molecular sieves for 24 hours at 60 °C for 24 hours. Lithium hexafluoroarsenate (LiAsF₆, LaRoche "Lectrosalt") was dried at 60 °C under vacuum, also for 24 hours. Lithium foil was used as received from Foote Mineral Company, and the Li-Al alloys were prepared by Cyprus Specialty Metal Company. Carbon dioxide (CO₂) was ultrahigh-purity bone dry from Matheson.

DISCUSSION AND RESULTS

The lithium cycling efficiency of an electrolyte was calculated based upon the amount of coulombs available at the working electrode (0.124 mm, 2.57 cm², which resulted in about 236 coulombs). This was determined by the weight of lithium used, and by

$$Q_{ex} = (F) (m)/MW, \quad (1)$$

where Q_{ex} = starting capacity of working electrode, coulombs; F = Faraday's constant, 9.649×10^4 coulombs/equiv; m = mass of Li working electrode, grams; and MW = molecular weight of Li, 6.941 g/mol.

A plate/strip cycle of 25.7 coulombs for each was performed (10 C/cm², 2.57 cm² area). The efficiency was calculated using

$$E = \frac{Q_s - \frac{Q_{ex}}{n}}{Q_s} \times 100, \quad (2)$$

where E = average lithium cycling efficiency, percent; Q_s = capacity stripped and plated, coulombs; Q_{ex} = starting capacity of working electrode, coulombs; and n = number of cycles obtained before Li depletion.

The relationship between the number of cycles achieved and the lithium cycling efficiency is presented in Fig. 3. Results are dependent upon various experimental factors, such as: solvent purification, cosolvent additives, solutes, solute concentration, substrate, electrode pretreatments, cell configuration, plating density, current density, rest periods between cycles, and temperature; i.e., various methods of solvent purification where the use of different dessicants and various fractionation techniques can be studied by this experiment. In addition, cosolvent additives, inorganic additives (or saturation with CO₂), and their effects on lithium cycling can be investigated. The possible benefits of electrode pretreatments, such as electrochemical, stripping, mechanical scraping, coating, or chemical treatment can be explored.

The importance of good lithium cycling efficiency is demonstrated in Table 1, where the values presented are the number of battery cycles expected, based solely on the available lithium. No efficiency loss is assumed with cycling at the cathode. For example, if a cell contained a 3/1 mole ratio of lithium to cathode, and if it is assumed that the cathode cycles with 100 percent efficiency, in order to achieve just 60 cycles, the electrolyte would require a lithium cycling efficiency of 95 percent. To keep the mole ratio of lithium low and still achieve extended cycle life, a lithium cycling efficiency of > = 98 percent is desired.

Data on some ester solvent electrolytes are reported in Tables 2 through 6. Lithium hexafluoroarsenate was the solute of choice and is used in all the electrolyte preparations. Experiments were all performed at 25°C. It was found that the cycling efficiency is independent of electrolyte conductivity, viscosity, density, and dielectric constant. Table 2 shows the properties

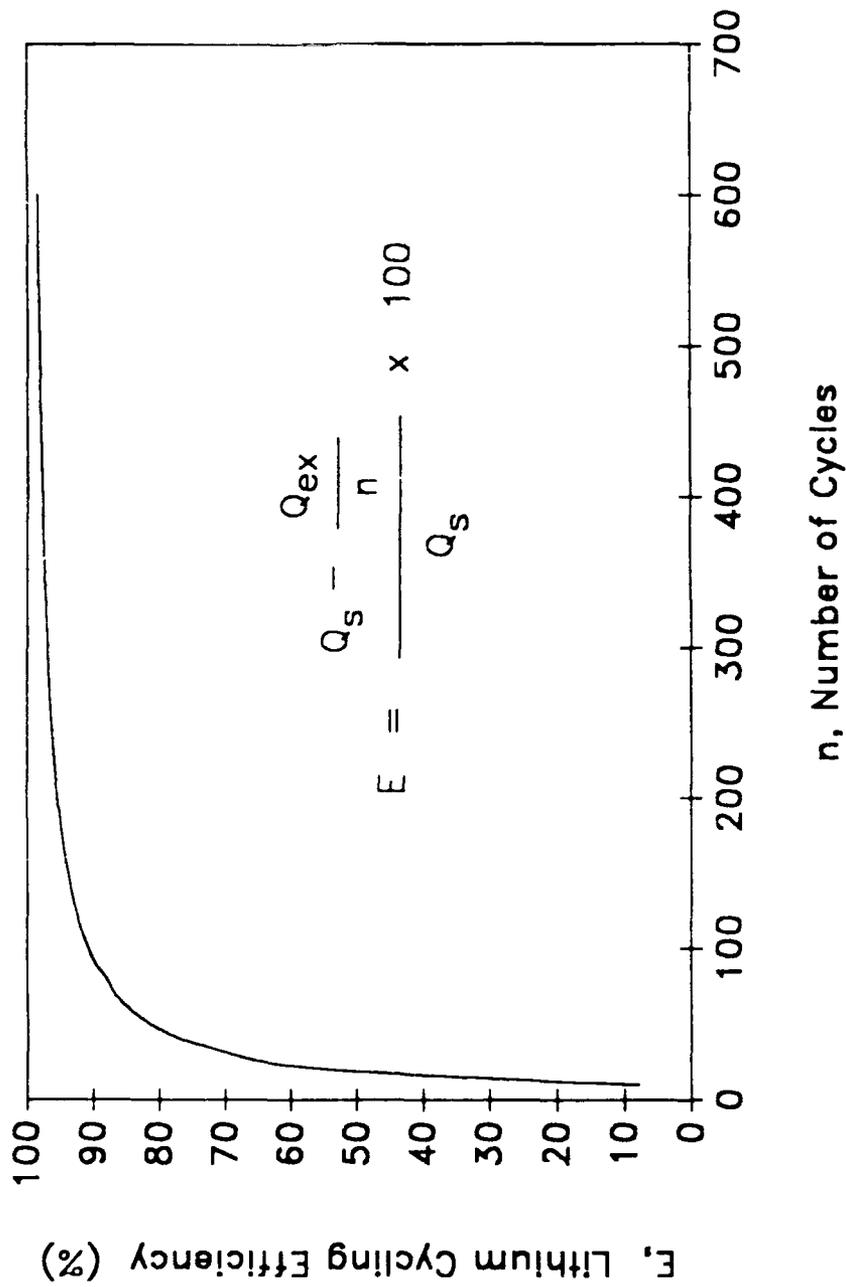


FIGURE 3. Relationship between the number of cycles achieved and the lithium cycling efficiency.

TABLE 1. Theoretical Cycle Life Based on Lithium

Li/Cathode Mole Ratio	Electrolyte Efficiency			
	85	90	95	98
1/1	7	10	20	50
2/1	13	20	40	100
3/1	20	30	60	150
4/1	27	40	80	200

TABLE 2. Properties of Electrolyte Solutions at 25°C

Electrolyte LiAsF ₆ (1.5-2.0m)	Electrolytic Conductance (10 ² S/cm)	Li Cycling Efficiency (%)
MF	4.7	71
MA	2.6	30
DMC	1.1	80
DEC	0.5	0

TABLE 3. Lithium Cycling Efficiency of Mixed Solvent Electrolytes.

Electrolyte LiAsF ₆ (1.5 - 2.0m)	Li Cycling Efficiency (%)
MF	71
75 mass% MF/DMC	76
50 mass% MF/DMC	84
25 mass% MF/DMC	85
DMC	80

TABLE 4. Lithium Cycling Efficiency of Ternary Solvent Electrolytes.

Electrolyte LiAsF ₆ (1.5 - 2.0m)	Li Cycling Efficiency (%)
MF	71
MF/DMC (3:1)	76
MF/DMC/EC (8:1:1)	85
MF/DMC/EC (16:3:1)	82

TABLE 5. Lithium Cycling Efficiency of Electrolyte with CO₂

Electrolyte LiAsF ₆ (1.5 - 2.0m)	Li Cycling Efficiency (%)
MF	71
MF/CO ₂	93
75 mass% MF/DEC	82
75 mass% MF/DEC/CO ₂	94

TABLE 6. Lithium Cycling Efficiency of Li-Al Anodes

Working Electrode	Electrolyte (1.7 - 1.9m LiAsF ₆)	
	MF	75% MF/DEC
Li	71	82
95% Li/Al	80	77
90% Li/Al	82	63

of some single-solvent electrolytes. The DMC, which has a low electrolytic conductivity, demonstrated the highest cycling efficiency with lithium. Improvement of the efficiency can be obtained when mixed solvent electrolytes, such as DMC in MF, are used. (See Table 3.) The trade-off is, although mixtures of MF and DMC improve the cycling efficiency, the conductivity decreases as DMC is added. Table 4 shows that further improvement was realized by adding EC to the MF/DMC mixtures; again, there is a trade-off. Besides lower conductivity, EC is a solid at room temperature and will limit the low-temperature performance of the electrolyte.

The addition of CO_2 greatly improved the stability of lithium in the electrolytes. Table 5 gives the cycling efficiencies for MF and MF/DMC with CO_2 . Saturation with CO_2 was achieved by filling the head space over the electrolyte with 25 psig of the gas for 24 hours. The exact mechanism of the interactions among CO_2 , the electrolyte, and lithium is very complex, and is still unclear. A beneficial reaction with the surface species on the lithium can occur, or a more stable film morphology may be formed.

In the pursuit of a more stable anode for rechargeable batteries, many substitutes have been investigated. Table 6 demonstrates the lithium cycling efficiency of two Li-Al alloys. It was observed that the efficiency increased in MF, but decreased in MF/DMC mixtures.

CONCLUSIONS

The highest lithium cycling efficiency obtained was 94 percent with 75 mass percent MF/DEC with CO_2 . This is still below the preferred goal of 98 percent for practical cells. With the trade-offs among cycle life, storage, electrolyte conductivity, and temperature of operation, and with the added requirement that the electrolyte be stable with the cathode, it can be concluded that an electrolyte that cycles lithium well, may or may not be a good battery electrolyte. The lithium cycling experiment was found to be a valuable screening tool when considering cycle life and the storage aspects of lithium battery electrolytes. To understand why certain electrolytes have good cycling efficiencies, and why others do not, a full understanding of the surface species and the film morphology is required.^{14,15}

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