Electrical Energy Storage and Intercalation Chemistry

Abstract. *The electrochemical reaction of layered titanium disulfide with lithium giving the intercalation compound lithium titanium disulfide is the basis of a new battery system. This reaction occurs very rapidly and in a highly reversible manner at ambient temperatures as a result of structural retention. Titanium disulfide is one of a new generation of solid cathode materials.*

We have recently reported on the fundamental properties of the Li_xTiS_2 series of intercalation compounds (*1–6*). Those studies were initiated by our finding that titanium disulfide could be used as the cathode of a high-energy-density reversible battery with a lithium anode (*7*). We report here on this relationship between intercalation chemistry and electrical energy storage.

The recent work on high-energy batteries, which are required for electric vehicle propulsion and for the storage of off-peak and solar power, has been reviewed by Cairns and Shimotake (*8*). The high operating temperatures of most of these batteries cause substantial corrosion problems that are not yet solved and will pose significant barriers to their acceptance by the general public. We therefore set out to determine whether an alkali metal–based battery couple could be found that would operate reversibly at ambient temperatures. For convenience, a lithium anode and an organic electrolyte were chosen, and a search was initiated for an electronically conductive, highly oxidizing solid that could react readily and reversibly with lithium as the cathode. It was also necessary that the solid be light in weight and inexpensive.

A group of materials that are known to be highly conductive are the layered dichalcogenides of the transition metals of groups IVB and VB of the periodic table. They have also aroused much interest because of their ability to intercalate a variety of molecules, such as pyridine, in the van der Waals layers of the structure and because of the effect of these inserted species on their superconductive properties, which has been described by Gamble *et al.* (*9*). However, nothing was known concerning the possibility of forming them in an electrochemical cell, or of the energy or reversibility of the reaction. We have shown that these intercalation complexes can be readily formed electrochemically at ambient temperatures; thus, for example, pyridine was inserted in a few minutes by the electrolysis of a solution of pyridinium hydrochloride at a TaS_2 electrode (*10, 11*). The direct reaction of pyridine with TaS_2 normally requires temperatures around 200°C and several days. The first indication that the free energy of formation of the alkali metal complexes was substantial came from the reaction of KOH with TaS_2 (*1*). In this reaction potassium surrounded by a ring of water molecules was intercalated; the water could be readily driven out by heating to 100°C. That the potassium did not reduce the water indicates a potential of K^+ of around 2 volts or more relative to potassium metal; this is in marked contrast to the corresponding compound of graphite, C_8K, where this potential is only 0.2 volt (*12*).

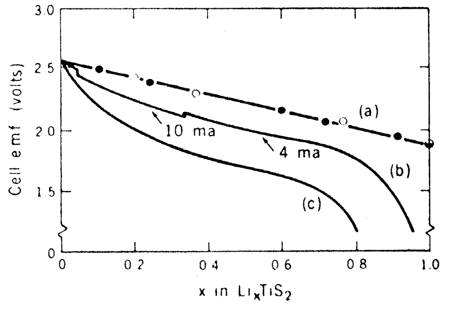
For cell testing we chose to use TiS_2, not only because it had the lowest weight and cost of all the layered dichalcogenides, but also because of its metallic conductivity, whose origin has undergone extensive study (*13, 14*). In addition, nuclear magnetic resonance studies (*4*) showed that lithium self-diffusion is most rapid in TiS_2 of all the layered sulfides. A simple electrochemical cell was thus set up in which the anode was lithium, the electrolyte $LiPF_6$ dissolved in propylene carbonate, and the cathode a single crystal of TiS_2. The cell electromotive force (emf) was 2.5 volts, a high value, as suggested by the hydration studies. On discharge, initial current densities of 10 ma per square centimeter of active crystal area were found; these are about an order of magnitude higher than those previously reported for any organic electrolyte battery system. These measurements indicate that the lithium diffusion coefficient is about 10^{-7} cm^2/sec. The emf of this cell on open circuit is shown by curve a in Fig. 1. The slope of this plot is indicative of a single-phase reaction represented by the equation

$$x\mathrm{Li} + \mathrm{TiS_2} \rightarrow \mathrm{Li_xTiS_2}$$

X-ray analysis of the discharge products showed that reaction proceeded by intercalation of the lithium into the TiS_2 lattice with a maximum expansion of the structure of 0.5 Å, ~ 10 percent, perpendicular to the basal planes (*5*). This was confirmed by x-ray analysis of $LiTiS_2$ (*3*) formed from *n*-butyl lithium and TiS_2 (*2*).

By starting with a cell with an $LiTiS_2$ cathode made from *n*-butyl lithium or a fully discharged electrode, curve a in Fig. 1 could be retraced exactly, indicating the complete reversibility of the system and the 100 percent coulombic efficiency of the TiS_2 electrode. To test the cell in a more realistic configuration, a mixture of finely divided TiS_2 and Teflon (9 to 1 by weight) was hot-pressed into a stainless steel grid of area 2 cm^2, surrounded by a polypropylene separator and a lithium anode, and immersed in an electrolyte consisting of $LiClO_4$ dissolved in a mixture of dimethoxyethane and tetrahydrofuran (30 to 70). The discharge characteristics of this cell at 10 and 4 ma are shown by curve b in Fig. 1. A cell was then shallow-cycled—operated at 4 percent of its full capacity—more than 1100 times and retained reversibility throughout, as shown by curve c in Fig. 1, which is a discharge curve after these cycles. The TiS_2 still maintained more than 70 percent of its theoretical capacity at this stage (based on the reaction $Li + TiS_2 \rightarrow LiTiS_2$), indicating the remarkable reversibility of TiS_2.

The current densities measured on the single crystal were confirmed in the powder cell configuration described above and the data obtained are shown in Fig.



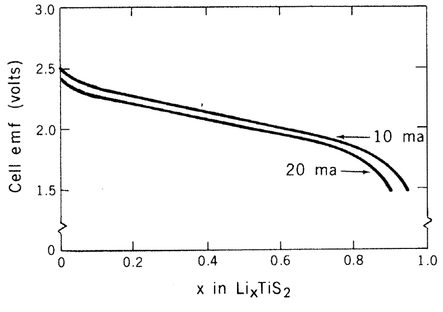


Fig. 1 (left). Cell emf of Li/TiS_2 couple. (Curve a) Open-circuit values obtained on discharge of (●) TiS_2 and recharge of (○) $LiTiS_2$, (curve b) values on discharge at 10 and 4 ma, and (curve c) values on discharge after the 1100 cycles at 4 ma. The differences between the curves are mainly due to the resistance losses in the electrolyte associated with a large electrode separation. Fig. 2 (right). Discharge characteristics in solution of lithium aluminum chloride in methyl chloroformate (*21*).

2. The current density for high utilization is optimized for low values of y in $Ti_{1+y}S_2$, because the excess titanium occupies sites in the van der Waals layers, impeding the diffusion of lithium by pinning the layers together (*3*). These currents are comparable to those obtained in the intermediate-temperature (200°C) $Na/SbCl_x$ molten salt cell (*15*). They are only slightly less than those used in the high-temperature (400+°C) lithium/metal-sulfide cells (*16, 17*), where, for example, CuS was cycled at 50 ma/cm^2, FeS_2 and FeS at 40 ma/cm^2, and NiS and Cr_2S_3 at 10 ma/cm^2. Even higher current densities may be obtained by using molten salts at elevated temperatures. These high currents and the ready reversibility of the reaction are directly associated with the crystal structure, which remains essentially unchanged during reaction; no chemical bonds are broken in the host TiS_2 matrix during the insertion or removal of lithium (*5*). Holleck *et al.* (*18*) studied these cells and found good reversibility but reported very low current densities, 0.33 ma/cm^2.

The energy density of the Li/TiS_2 couple is found from Fig. 2 to be 480 watt-hour/kg, which is comparable to the energy densities calculated for Na/S cycling in the single-phase region and the LiAl/FeS high-temperature cells now under development. The values for the latter are 330 and 460 watt-hour/kg, respectively, and are anticipated to reach 100+ watt-hour/kg in practical cell configurations. As the TiS_2 ambient-temperature cell will require less deadweight associated with heat insulation and corrosion-resistant materials, it should also fall in this area, making it feasible for electric vehicle propulsion. Preliminary calculations and extended high-current operation near full capacity indicate that the required power densities are achievable with the TiS_2 cell (*19*).

In conclusion, TiS_2 has a high energy density and rate capability when coupled with a lithium anode, a high electrical conductivity, and a discharge-charge mechanism involving intercalation of lithium between the layers of the host's crystal structure that permits extended reversibility (*7*). Moreover, in contrast to most oxidants such as Cl_2, TiS_2 has a kinetically selective oxidizing power, making it highly reactive to species that can be intercalated but noncorrosive to its environment. This couple has potential as an ambient-temperature, as well as high-temperature, battery for electric vehicle propulsion. The Na/TiS_2 couple is less interesting because of the much greater free energy change with x (*20*) and the presence of a number of crystalline phases, which places an upper limit of ~0.8 on x at 25°C (*6*).

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References and Notes

1. M. S. Whittingham, *Mater. Res. Bull.* **9**, 1981 (1974).
2. M. B. Dines, *ibid.* **10**, 287 (1975); U.S. Patent No. 3,933,688 (1976).
3. M. S. Whittingham and F. R. Gamble, *Mater. Res. Bull.* **10**, 363 (1975).
4. B. G. Silbernagel, *Solid State Commun.* **13**, 1911 (1975).
5. M. S. Whittingham, *J. Electrochem. Soc.* **123**, 315 (1976).
6. B. G. Silbernagel and M. S. Whittingham, *Mater. Res. Bull.* **11**, 29 (1976).
7. M. S. Whittingham, Belgian Patent No. 819,672 (1973).
8. E. J. Cairns and H. Shimotake, *Science* **164**, 1347 (1969).

→ F. R. Gamble, J. H. Osiecki, M. Cais, R. Pisharody, F. J. DiSalvo, T. H. Geballe, *ibid.* **174**, 493 (1971).

10. M. S. Whittingham, *Chem. Commun.* (1974), p. 328.
11. G. V. Subba Rao and J. C. Tsang, *Mater. Res. Bull.* **9**, 921 (1974).
12. S. Aronson, F. J. Salzano, D. Bellafiore, *J. Chem. Phys.* **49**, 434 (1968).
13. A. H. Thompson, F. R. Gamble, C. R. Symon, *Mater. Res. Bull.* **10**, 915 (1975).
14. A. H. Thompson, *Phys. Rev. Lett.* **35**, 1786 (1975).
15. J. Werth, I. Klein, R. Wylie, *J. Electrochem. Soc.* **122**, 265C (1975).
16. L. Heredy and L. R. McCoy, U.S. Patent No. 3,898,096 (1975).
17. D. R. Vissers, Z. Tomczuk, R. K. Steunenberg, *J. Electrochem. Soc.* **121**, 665 (1974).
18. G. L. Holleck, F. S. Shuker, S. B. Brummer, in *Proceedings of the 10th Intersociety Energy Conversion Engineering Conference, Newark, Delaware, August 1975* (Institute of Electrical and Electronics Engineers, New York, 1975).
19. L. H. Gaines, preprint.
20. D. A. Winn, thesis, Imperial College (1975).
21. This electrolyte is susceptible to decomposition on overdischarge and so is not suitable for commercial use. The cell was, however, deep-cycled—operated at >58 percent of capacity—at these rates for 16 cycles before any apparent degradation set in.
22. I would like to thank F. R. Gamble for introducing me to the layered sulfides and for his constant encouragement. In addition I gratefully acknowledge the help of my colleagues, R. R. Chianelli, M. B. Dines, B. G. Silbernagel, A. H. Thompson, R. W. Francis, L. H. Gaines, G. H. Newman, and B. M. L. Rao.

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Masses of the Galilean Satellites of Jupiter

Abstract. *Numerical data derived from the observation of the four great satellites of Jupiter are compared with the values obtained through Sampson's theory by using the new JPL (Jet Propulsion Laboratory) system of masses. It is not possible to fit the coefficient of the free oscillation in the longitude of Ganymede, whose argument is* $l_3 - \tilde{\omega}_4$ *(the mean longitude of Ganymede referred to the proper apse of Callisto), and the mass of Callisto derived from the path of Pioneer 10.*

The theory of the four great satellites of Jupiter—Io, Europa, Ganymede, and Callisto—involves almost 30 integration constants and physical parameters. These physical parameters are the masses of the satellites and the coefficients of the main zonal harmonics of Jupiter's field of gravitation. In classical theories they have been determined from observations simultaneously with the orbital elements. Today, study of the motions of space probes flying in the neighborhood of Jupiter allows these parameters to be determined independently. The first determination, performed at Jet Propulsion Laboratory (JPL), Pasadena, California, was made by analyzing the Doppler shift of the signals emitted by Pioneer 10 when it was near Jupiter (*1*). These results and the classical results of Sampson (*2*) and De Sitter (*3*) are shown in Table 1; they allow, for the first time, an objective comparison between some parts of the works of Sampson and De Sitter. In order to make this comparison we use the formulas given by Sampson in his theory (*2*, p. 173) and the JPL system of physical parameters to calculate some quantities that were determined by both from the observations. They are:

1) The coefficient of the induced equation of the center in the longitude of Io;

2) The coefficient of the induced equa-

Table 1. Modern and classical determinations of satellite masses and Jupiter gravity harmonics (J_2 and J_4). Abbreviation: R_{Eq} is the equatorial radius of Jupiter.

Parameter	JPL (*1*)	Sampson (*2*)	De Sitter (*3*)
Mass ($\times 10^{-5}\, m_{Jup}$)			
m_1 (Io)	4.696 ± 0.06	4.497	3.81 ± 0.45
m_2 (Europa)	2.565 ± 0.06	2.536	2.48 ± 0.1
m_3 (Ganymede)	7.845 ± 0.08	7.988	8.17 ± 0.15
m_4 (Callisto)	5.603 ± 0.17	4.504	5.09 ± 0.6
$J_2 R_{Eq}^2$ ($\times 10^6$ km)	75.04 ± 0.2	75.73	75.07 ± 1.5
J_4 ($\times 10^{-6}$)	−650 ± 150		690