OVERCHARGE PROTECTION IN Li-ALLOY/METAL DISULFIDE CELLS

Laszlo Redey
Argonne National Laboratory
Chemical Technology Division
9700 S. Cass Avenue, Argonne, IL 60439

ABSTRACT

Charge and overcharge reactions of FeS\textsubscript{2}, NiS\textsubscript{2}, and (Fe-Ni)S\textsubscript{2} electrodes were studied in half-cell and full-cell experiments to investigate the electrochemical stability of these materials at high charge potentials. In Li\textsubscript{2}S-saturated (LiCl-KCl, LiF-LiCl-LiBr, and LiCl-LiBr-KBr) electrolytes, a new plateau appeared at 2.05-2.1 V vs. Li-Al and was associated with polysulfide anion formation. The polysulfide seems to stabilize the transition-metal sulfides against overcharge-related dissolution, even at 2.2 V. The anodically formed polysulfide provides overcharge tolerance for Li-alloy/MS\textsubscript{2} cells by an electrochemical-chemical sulfide/polysulfide cycle.

BACKGROUND

The present Li-alloy/metal sulfide cells require voltage-limited charge termination. An experimentally determined limit (about 1.9 to 2.05 V for the Li-alloy/FeS\textsubscript{2} cells [1,2]) is set to prevent unwanted electrode reactions. Although both the negative and the positive electrodes are affected by this problem, only those problems that are associated with the latter are discussed in this paper. Above the voltage limit, if the charge is continued, detrimental overcharge reactions occur, such as soluble transition-metal salt formation from the active material and anodic dissolution of the current collector. Overcharge reactions of the metal sulfide electrodes have been studied extensively [3-6], and a review on this topic is available [7]. The overcharge reactions shorten cell life to a great extent by decreasing capacity and causing metal to precipitate in the separator, which then short circuits the electrodes. The deleterious effect of the overcharge reactions is proportional to the charge applied above the critical voltage limit.

Overcharge of the weak cells of a battery is a serious problem whenever the utilizable capacities of the cells become uneven. Maintaining the charge voltage at or below the voltage limit and simultaneously reaching equal capacity in each serially connected cell of a metal sulfide battery over many cycles are difficult tasks. To overcome this difficulty, a special integrated charger-battery system...
has been developed [8]. This system, which has interconnections between each cell and the charger, removes any cell from charge individually that reaches the charge voltage limit.

Ideally, the battery overcharge control, however, should rely on a built-in chemical mechanism that furnishes the cells with an inherent overcharge tolerance. A similar mechanism is available in lead-acid and Ni-Cd cells.

EXPERIMENTS AND RESULTS

To explore the possibility of chemical overcharge protection, charge and overcharge reactions of FeS₂, NiS₂, and (Fe-Ni)S₂ electrodes in 58% LiCl - 42% KCl eutectic, 22% LiF - 31% LiCl - 47% LiBr all-Li⁺-cation, and 25% LiCl - 37% LiBr - 38% KBr "low melting" electrolytes (composition in mol%) were studied by intermittent galvanostatic cycling. The electrolytes were Li₂S-saturated, i.e., they contained more sulfide than the stoichiometrically needed quantity to form the heavy-metal disulfides from their respective metals.

Two sets of experiments were carried out: (i) half-cell experiments to study the charge properties of the sulfides and (ii) full-cell experiments to investigate the interaction between the positive and negative electrode in an arrangement that simulates the conditions of the compact engineering cells. Details of the cell design and the method used in the half-cell study are described elsewhere [9,10]. For the full-cell study, a sulfide electrode was combined with a Li-alloy negative electrode into a cell sandwich; this cell was designed for performing experiments under a wide variety of conditions, including open and sealed operations. Both types of cells were cycled, at least, 50 to 150 times before the experiment was terminated.

The half-cell experiments revealed a new plateau at about 2.05-2.1 V vs. Li-Al (IR-free closed-circuit value). This potential range had been considered to be beyond the safe charge voltage limit and subject to detrimental overcharge reactions. The half-cell experiments suggested an electrode reaction at 1.95-2.1 V potential that was not directly related to the transition-metal sulfide process because (i) the charge passed during this plateau was not recoverable in the subsequent discharge, (ii) the recoverable useful discharge capacity of the transition-metal sulfide was hardly affected by the length of the overcharge plateau, and (iii) the useful discharge capacity did not decline in the following cycles, even after several overcharging cycles. The results in Table 1 show the charge and discharge capacities of an FeS₂ electrode before, during, and after "overcharge" (i.e. when the electrode potential is higher than 1.9 V).
Similar results were obtained in the full-cell experiments with the three listed metal disulfides. Figure 1 shows the voltage variation of a Li-Al-Si/(Fe-Ni)S$_2$ sealed cell when cycled between discharge and charge voltage limits of 1.0 and 2.1 V, respectively. The voltage oscillations seen on the curve are traces of the voltage excursions during 15-s current interruptions, which were applied regularly to measure area-specific cell impedance [10]. In the 21st charge (C-21), when the voltage limiter relay was inactivated, the cell was overcharged with a current density of 50 mA/cm$^2$ to approximately 2.5 times the theoretical capacity. In spite of this unusual treatment, no damage occurred in the electrodes. This observation is substantiated by the fact that the plot recorded in the pre-overcharge cycle is unaltered from that obtained in the subsequent cycles. Furthermore, the cell showing good capacity retention performed many more cycles and several overcharges.

DISCUSSION

Both the half-cell and full-cell experiments suggested that transition-metal disulfide electrodes in Li$_2$S-saturated electrolyte will undergo beneficial overcharge reactions that provide overcharge tolerance.

The mechanism of the overcharge tolerance can be explained by the action of an electrode reaction-chemical reaction (ER-CR) cycle. At high positive potentials, the abundant S$^{2-}$ ions of the electrolyte are oxidized to polysulfide on the sulfide electrode in the electrode reaction

$$\text{xS}^{2-} \rightarrow \text{S}_x^{2-} + 2(x - 1)e^- \quad (1)$$

where x < 2. Then, the polysulfide, after having been diffused to the negative electrode, is reduced back to sulfide on the Li alloy in the chemical reaction

$$\text{Li}_2\text{S}_x + 2(x - 1)\text{Li}^0 \rightarrow x\text{Li}_2\text{S} \quad (2)$$

The symbol Li$^0$ in Eq 2 represents the excess lithium content of the alloy that is produced during the overcharge. The sulfide produced in Eq. 2 diffuses and migrates back to the positive electrode and short circuits the ER-CR cycle. Although the polysulfide and the excess lithium in the alloy are produced continuously during overcharge, they do not accumulate to an unacceptably high level because the counteracting chemical reaction, when steady state is reached, consumes them at the same rate as that of their formation. The high solubility of the polysulfide assures a high diffusion rate and, therefore, fast consumption at the negative electrode. Consequently, the ER-CR cycle can maintain a self-regulated charge voltage limit, which is set by the current density and temperature.
A key element of the proposed ER-CR cycle is that the polysulfide formation takes over the charge transfer from the transition-metal sulfide electrode reactions, thus providing an electron source for the inert-metal current collector while the overcharging current is flowing.

Previous findings support the polysulfide formation under the conditions of our experiments. Cyclic-voltammetric experiments indicated that Li$_2$S was readily oxidized in various complicated anodic reactions on inert electrodes to various polyanions of sulfur in the potential range of 1.9 to 2.2 vs. Li-Al [11,12]. The lower end of this range coincides with the potential of the FeS$_2$ formation [12]. However, because the FeS$_2$ formation takes place at high overpotential [12], the polysulfide anion formation is energetically favored relative to the transition-metal disulfide formation. The polysulfide may eventually help the FeS$_2$ formation from the lower sulfur activity phases in a chemical interaction. This reaction mechanism would explain the observed [13] good charge acceptance and high utilizations of the disulfide electrodes in Li$_2$S-saturated electrolytes.

The term disulfide is used in this paper only in the generic sense, indicating the transition-metal sulfide phase(s) of highest sulfur activity; the actual compound present at the end of the charge is not known. The surplus of Li$_2$S in the described experiments may dictate a phase transformation sequence that is different from the presently known one [12] that is valid for the disulfides at 4Li:Fe:2S atom ratio.

CONCLUSION

Identified in this work was an effective overcharge mechanism that protects the transition-metal disulfide electrodes in Li$_2$S-saturated electrolyte against anodic dissolution and sets a self-regulated charge voltage limit. The resulting overcharge tolerance of the cells, which is believed to be due to the ER-CR cycle, should eliminate the need of voltage-limited cell charge and allow the use of standard cyclers for charge equalization in cells of the battery. This would reduce the initial and operating cost of Li-alloy/MS$_2$ batteries.

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Table 1. Charge/Discharge Imbalance of FeS$_2$ Electrode$^a$

| Cycle No. | Charged$^b$ (mAh) | Overcharged$^c$ (mAh) | Cut-off V vs. Li-Al | Discharged$^d$ (mAh) |
|-----------|-------------------|----------------------|---------------------|---------------------|
| 128       | 325               | 0                    | 1.90                | 320                 |
| 129       | 322               | 0                    | 1.90                | 321                 |
| 130       | 320               | 215                  | 2.15                | 327                 |
| 131       | 315               | 280                  | 2.20                | 325                 |
| 140       | 323               | 170                  | 2.15                | 317                 |
| 141       | 325               | 310                  | 2.20                | 330                 |
| 142       | 321               | 0                    | 1.90                | 317                 |
| 150       | 325               | 0                    | 1.90                | 315                 |

$^a$ All-Li$^+$-cation electrolyte, 100 mA/cm$^2$, 475$^o$ C
$^b$ Charged to 1.90 V
$^c$ Measured above 1.90 V
$^d$ Discharged to 1.5 V

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Figure 1. Evidence of Overcharge Tolerance in Cycle 21

Cell voltage, mV

Time from C-20 to D-23, h

Li-Al-Si/(Fe-Ni)S$_2$ cell, 385$^o$ C, 50 mA/cm$^2$