

FACTORS AFFECTING NICKEL-OXIDE ELECTRODE
CAPACITY IN NICKEL-HYDROGEN CELLS

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The nickel-oxide electrode common to the nickel hydrogen and nickel cadmium cell is by design the limiting or capacity determining electrode on both charge and discharge. The useable discharge capacity from this electrode, and since it is the limiting electrode, the useable discharge capacity of the cell as well can and has been optimized by rate of charge, charge temperature and additives to electrode and electrolyte. Recent tests at COMSAT Labs with nickel hydrogen cells (Ref. 1) and tests performed almost 25 years ago with nickel cadmium cells (Ref. 2) indicate an improvement of capacity as a result of using increased electrolyte concentration.

The capacity attainable from the nickel oxide electrode and hence from the nickel-hydrogen (and nickel cadmium) cells depend on how effectively and extensively the electrode can be charged. Full charge or the conversion of all active material to a higher valence state is extremely difficult to achieve under spacecraft flight conditions where there are rate, time, and temperature constraints on charge. The difficulty in charging the nickel-oxide electrode is due to the occurrence of a competing parasitic reaction involving the evolution of oxygen at approximately the same potential as that of the charging reaction of the nickel-oxide electrode. The two reactions and their open circuit potentials as well as the relative effect of current density and the temperature on potentials are shown in Figure 1.

At reversible (extremely low current densities) conditions a nickel hydrogen cell would never be charged because 81mv more voltage is required to charge the nickel-oxide electrode than to evolve oxygen in alkaline media. Because of the relative effect of temperature and charge current density on the potentials of these two reactions, it has been possible to combine these parameters so that the charge reaction predominates over the parasitic evolution of oxygen (Figure 1).

Within the practical limits of cell charging; between 1 and 10 ma/cm.²; the voltage-current density curves favor the charging of the nickel electrode (Figure 2). The

temperature-voltage coefficient for the oxygen evolution and that of nickel oxide charging reaction are both negative, however, that of the oxygen evolution is more negative (Figure 2). Therefore, a decrease in temperature would result in relative voltages favoring the charging of the nickel electrode. The effect of decreasing temperature and increasing charging rate to improve the efficiency of nickel hydrogen and nickel cadmium cells is well known and has been empirically applied by users of these alkaline systems for many years.

The thermodynamic effect of varying the KOH concentration is common to both the nickel electrode charging and the oxygen evolution reaction, nevertheless, a significant increase in available capacity has been noted as a result in increasing electrolyte concentration under constant condition of overcharge. (Ref. 1)

Figure 3 shows capacities obtained with nickel hydrogen cells at 0° and 20°C. The cells are identical except for their electrolyte concentrations. The capacities obtained at both temperatures are almost in linear proportion to electrolyte concentration.

The effect of increased electrolyte concentrations seems to be the same on the relative potentials of the nickel-oxide vs and parasitic oxygen evolution as that observed for decreasing temperature and increasing charge current. Thus there is an additional parameter which can be varied to create the most favorable conditions for nickel electrode cell charge acceptance.

Figure 4 shows plots of nickel hydrogen cell pressure vs. charge input for the cells whose capacities are shown in Figure 3. When the positive electrodes in a nickel hydrogen cell evolve oxygen, hydrogen and oxygen react causing a decrease in the slope of pressure vs. Ah input. When all of the charging current is used for oxygen evolution, all hydrogen evolved at the negative electrode is consumed and the cell pressure remains constant as charge continues.

As shown in Figure 4, the cells with the highest electrolytes concentration accept the most charge prior to pressure plateau indicating the greatest charge acceptance prior to predominant oxygen gassing.

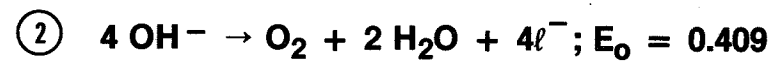
The effect of electrolyte concentration on cell and electrode capacities may also have frequently been demonstrated by the capacity differences reported for flooded electrode tests and for the same electrodes as part of electrolyte starved cells. Flooded capacities have generally exceeded cell capacities by about 15 to 20%. It is widely accepted that nickel oxide electrodes absorbs KOH from the electrolyte during

charge and at the same time yields water to the electrolyte. The equations shown in Figure 5 are only one representation of what is believed to occur during the charge of a nickel oxide electrode (Ref. 3). COMSAT Lab has developed data for nickel hydrogen cells which indicate a 10% decrease in electrolyte concentration when a cell is taken from complete discharge to full charge (Ref. 4).

The extent of decrease in electrolyte concentration as a result of charge is a function of ampere hours charged per unit volume of electrolyte. In a flooded condition the ampere hours of charge per unit volume of electrolyte is considerably smaller than that of a cell, therefore the decrease in KOH concentration will also be considerably less for electrodes charged in flooded electrolyte conditions than in case of the same electrodes contained in an electrolyte starved cell. Therefore, the electrodes in a flooded condition will accept more charge prior to gassing oxygen than the same electrode charged in a limited electrolyte volume cell as a result of the greater decrease in electrolyte concentration in the case of a cell.

The charge acceptance of a cell can be affected by both electrolyte concentration and volume. Electrolyte can therefore be considered a variable for improving charge efficiency and utilization in a N_1-H_2 cell and adds another dimension to charge management of these cells and batteries. By appropriate increase of electrolyte concentration and/or volume, a lower charge current and/or higher temperature, can be used resulting in smaller batteries and smaller charge arrays. This will impact weight and cost of a spacecraft. With respect to the effect of electrolyte concentration on life, data exists for geosynchronous orbit application, which indicates no adverse effects on battery life in the range of electrolyte concentrations investigated.

- References:
- (1) M. Earl - COMSAT Laboratories Technical Note PSD-83-029.
 - (2) L. Belove and I. M. Schulman - Proc. Ann Power Sources Conference 13, 82 1959.
 - (3) Bourgault and Conway - Can. J. Chem 38, 1557 (1960).
 - (4) J. F. Stockel - COMSAT Laboratories Technical Memo PSD-83-002.



$$\frac{\Delta E_2}{-\Delta T} > \frac{\Delta E_1}{-\Delta T}$$

$$\frac{\Delta E_2}{\Delta \ln i} > \frac{\Delta E_1}{\Delta \ln i}$$

Figure 1. Effect of temperature and current density on charging reaction (1) and parasitic reaction (2).

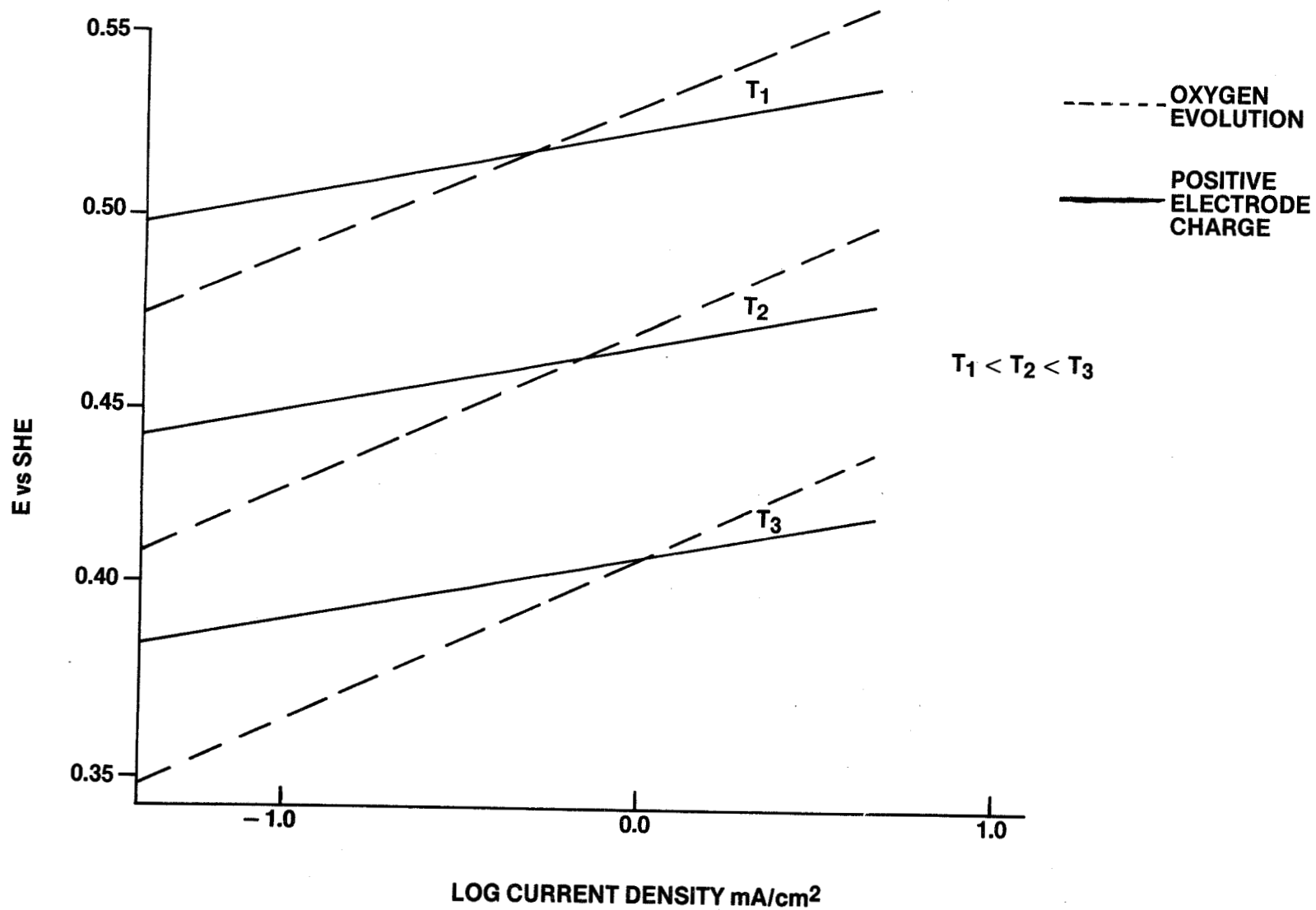


Figure 2. Charge efficiency as related to charge rate and temperature.

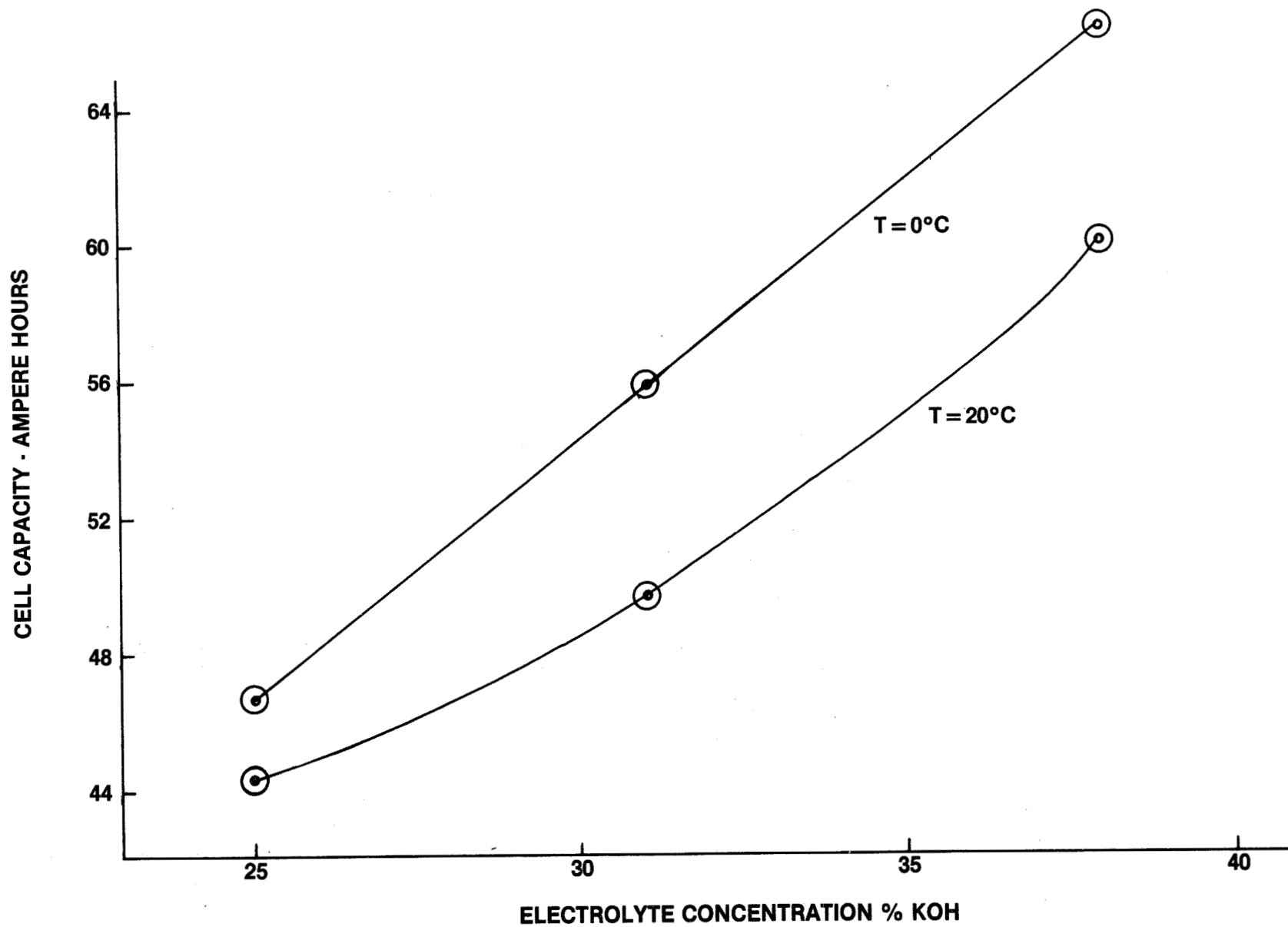


Figure 3. Nickel-hydrogen cell capacity vs. electrolyte concentration.

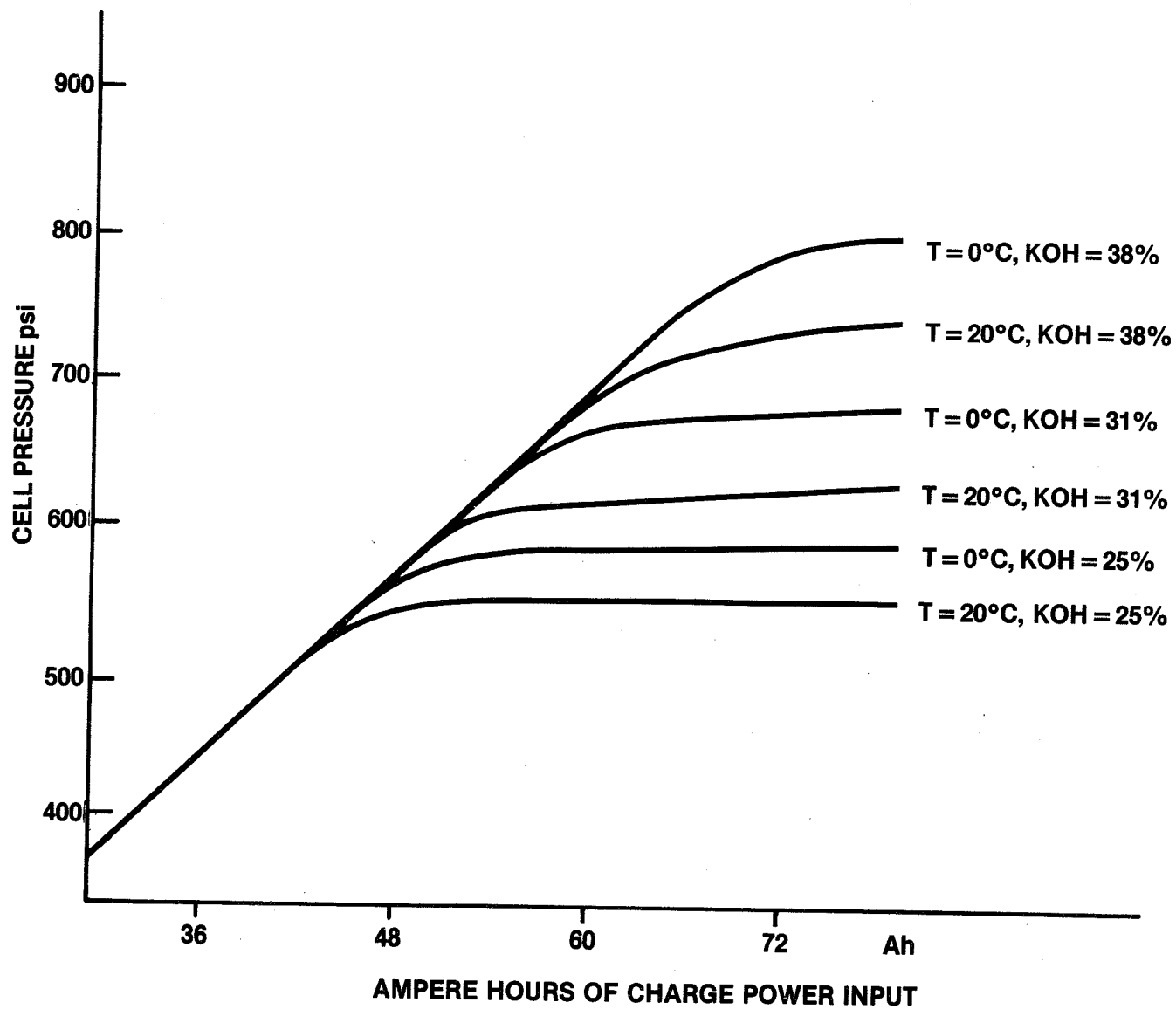


Figure 4. Nickel-hydrogen cell pressure vs. charge input as a function of electrolyte concentration and temperature.

THE CONCENTRATION OF KOH DECREASES AS THE STATE OF CHARGE OF A CELL INCREASES; AS A RESULT OF KOH ABSORBED BY THE CHARGED POSITIVE, AND H₂O RELEASED FROM THE DISCHARGED POSITIVE ACTIVE MATERIAL.

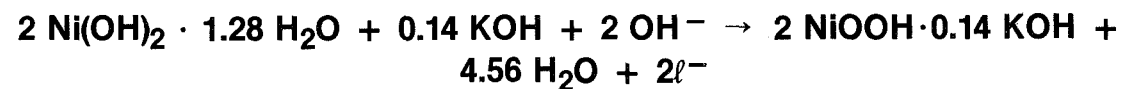


Figure 5. KOH concentration vs. state of charge.

- A. Thaller, NASA/Lewis Research Center: I take it Paul that the benefits are related to using higher concentrations of KOH rather than using nickel hydrogen?
- Q. Ritterman, Comsat: Beg your pardon?
- Q. Thaller, NASA/Lewis Research Center: The benefits were they related to using higher concentrations of KOH or benefits of using nickel hydrogen?
- Q. Ritterman, Comsat: I don't know why you are comparing concentration with system you can combine these. You can use these in both nickel hydrogen and nickel cadmium but I am talking primarily about nickel hydrogen because you have greater flexibility as far as current density and temperature goes. You are not limited by cadmium in nickel hydrogen.
- Q. Green, RCA-Astro: Paul, would the life expectancy of the nickel hydrogen battery increase with the KOH concentration that you've described?
- A. Ritterman, Comsat: Yes. Okay. There have been cells that have run for accelerated life test of 30 seasons at TRW with an end of discharge KOH concentration in excess of 38%. So within the range that I've talked about there has been reported no other problems in relation to life expectancy.
- Q. Green, RCA-Astro: No problem?
- A. Ritterman, Comsat: No problem.
- Q. Milden, Aerospace Corporation: The choice of the 31 or 32% electrolytes was over the years an optimum or a trade off between voltage characteristics and everything else, how would you suspect or expect the voltage on charge and discharge to vary with the increased concentration and also the effects of swelling and all other kinds of good stuff like that with a varied concentration. In other words, is this all good or is there a trade-off?
- A. Ritterman, Comsat: So far it looks like all good. I guess some more specific test would have to be done to determine the effect on swelling. But I think life data shows that you can sustain certainly at the end of discharge with a concentration as high as 40%.
- Q. Unidentified: What I'm saying Paul, when the current was higher the difference between the end of discharge voltages was higher?

- Q. Ritterman, Comsat: Yeah. Was it all the way through on the discharge?
- A. Unidentified: It was more pronounced toward the end. At the very beginning they were a little closer but they spread out as the discharge went on.
- Q. Unidentified: For the same amp output?
- A. Ritterman, Comsat: I can't answer that.

COMMENT

Unidentified: This is a comment. There are two points coming out of this session. One point is when you are talking about nickel cadmium or nickel hydrogen there are significant changes in the electrolyte concentration between charge and discharge. There are also significant differences in the variation in the KOH concentration of one to the other because the reaction that's taking place during that time of discharge. The other point is that there are different nickel hydrogen systems in operation using different levels of KOH concentration. And one other thing that Paul has pointed out very nicely in his paper is that there is a significant impact on cells performance as a result of KOH concentration.

Ritterman, Comsat: Yes I guess I didn't make my point clear about nickel cadmium and nickel hydrogen. In nickel hydrogen you really have no net change in hydroxide due to compound formulation but you do have a change in absorption of water and KOH concentration. But I didn't want to limit this to nickel hydrogen I think it's applicable to nickel cadmium cells.

Hendee, Telesat Canada: Basically the comment you made was the one I was going to make. You have to be careful about translating this into nickel cadmium as well. One of the reasons for the 31 to 32% was the nylon separator was it not? The degradation of the nylon separator was shown to be the least around a 31 or 32% KOH concentration. If you can change that you have a new ball game.

- Q. Rogers, Hughes Aircraft Corporation: Paul, I'm wondering the test data that you presented is that what we got after building the cells at Hughes or is additional data which is the same basically as what I remember we got?
- A. Ritterman, Comsat: The initial data about the effective concentration was found sometime prior to the Hughes testing.
- A. Ritterman, Comsat: Yes these cells are 48 amp per hour cells.