

Short Communication

Impedance of nickel/cadmium cells with nylon separator hydrolysate

M.S. Suresh

Battery Division, ISRO Satellite Centre, Airport Road, Vimanapura, Bangalore - 560017 (India)

(Received September 13, 1993; accepted January 13, 1994)

Abstract

In sealed nickel/cadmium cells, degradation of the nylon separator leads to decrease in the electrolyte and, eventually, to shorting of the cells. To understand this effect further, a study of the influence of nylon hydrolysis on the impedance of nickel/cadmium cells has been undertaken. Measurements have been made of the impedance of a positive-limited nickel/cadmium cell (flooded type) with and without nylon hydrolysate. The nylon hydrolysate was expected to affect the double-layer impedance of the nickel oxide electrode around a cell voltage of 0.4 V. Unfortunately, the results show only small changes in the cell impedance due to nylon hydrolysate and these are not considered to be significant. It appears, therefore, that the impedance technique does not provide unequivocal information about nylon hydrolysis.

Introduction

The nylon separator is an important component in nickel/cadmium cells. The separator degrades with use by undergoing hydrolysis in the potassium hydroxide electrolyte. It is well known that in sealed nickel/cadmium cells a separator weight loss of 10% is sufficient to cause internal shorting [1]. Hence, it is necessary to measure (or at least to detect) the separator hydrolysis by a non-destructive method.

When the nylon separator in a nickel/cadmium cell hydrolyses, the resulting products contain long hydrocarbon chains that may adsorb on the electrode surface. If such adsorption does occur, then it may be possible to detect the effect by a change in the double-layer impedance and the hindrance it may cause to the faradaic reactions that take place at the electrode. The kinetics of the electrode reactions can be measured non-destructively in a sealed cell by measurement of the impedance. Thus, an impedance technique was adopted to determine whether nylon hydrolysis can be measured in nickel/cadmium cells.

The impedance of sealed nickel/cadmium cells is composed of contributions from the positive electrode, the negative electrode, and the interelectrode region. Thus, the conditions for impedance measurement must be chosen in such a way that the contributions from the two electrodes can be separated from each other. It has been

shown [2] that the impedance of sealed nickel/cadmium cells at low states-of-charge ($<0.1\%$) is practically due to the nickel oxide electrode. It has also been demonstrated that around a cell voltage of 0.0 V, the cell impedance is due to the hydrogen-evolution reaction (HER) at the nickel oxide electrode; for a cell voltage of 0.3 to 0.7 V, the cell impedance is due to the double-layer at the nickel oxide electrode/electrolyte interface [2]. Hence, impedance measurements were made at low states-of-charge on an experimental nickel/cadmium cell.

Experimental

In order to study the effect of nylon hydrolysis on the impedance of nickel/cadmium cells, a temporary cell was constructed from one impregnated sintered positive plate and two negative plates (aerospace grade), each with a capacity of approximately 2 Ah. The electrodes were housed in a stainless-steel container with negative electrodes on either side of the positive electrode, and filled with 30% KOH electrolyte. Care was taken to avoid contact with nylon material, and the plates were washed thoroughly in double-distilled water. This constituted a positive-limited cell with a design similar to that of sealed nickel/cadmium cells.

The temporary cell was conditioned by two charge and discharge cycles with sufficient overcharge to ensure that the negatives were completely charged. The cell was then discharged across a 0.5Ω load to 10 mV and was dead-shorted for 24 h to reach a very low state-of-charge of the positive electrode. The negative electrode at this time was at approximately 50% state-of-charge as in sealed nickel/cadmium cells. The impedance of the cell was measured in the cell voltage range 0.0 to 1.2 V in steps of 0.1 V. At each cell voltage, the impedance was measured in the series-equivalent form ($R_s \pm jX_s$) by applying a signal of 1 mV (r.m.s.) in the frequency range 20 to 0.01 Hz. The impedance was directly measured using a Solartron frequency response analyzer and electrochemical interface. First, the impedance of the cell and the positive electrode was measured separately at 0.0, 0.5 and 1.2 V. The results confirmed that the cell impedance was practically due to the positive electrode. The small differences were due to the electrolyte resistance which can be easily accounted for in the measurements.

It has been shown that nylon separator loses about 10% of its weight by hydrolysis in KOH in about 15 h at 100 °C [3]. Thus, to prepare nylon hydrolysate, a separator material of 100 cm² area (type pellen 2505) was boiled in 30% KOH for 4 h. The expected weight loss was about 2.5%. The nylon extract, thus prepared, was added to the electrolyte of the temporary cell. Care was taken to avoid carbonation of KOH. The impedance of the temporary cell with nylon hydrolysate was measured at a cell voltage between 0.0 and 0.7 V, as before.

Results and discussion

The impedance of the cell was measured as $R_s - jX_s$. The values of R_s and X_s are plotted in Figs. 1 to 3 as a function of cell voltage at 1, 0.1 and 0.01 Hz, respectively, before and after the addition of nylon hydrolysate to the electrolyte. The general shape of the plots does not change, even though R_s and X_s tend to have a slightly higher value when nylon hydrolysate was added. Above about 0.5 V, no significant difference is observed in the impedance between the two conditions.

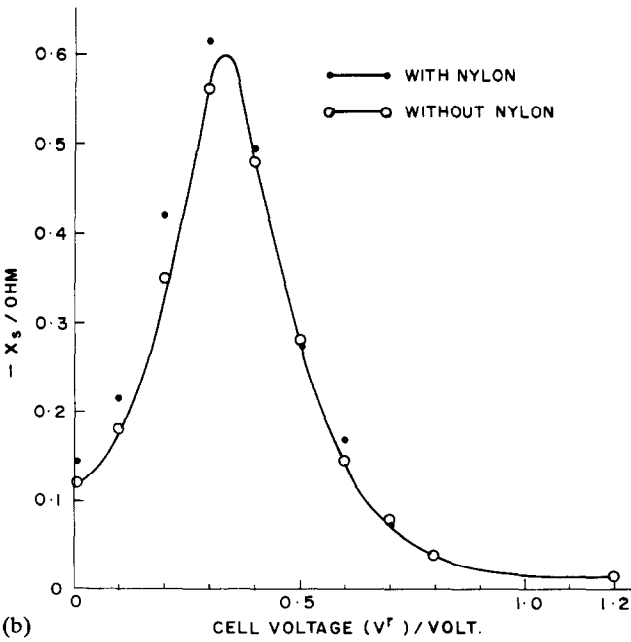
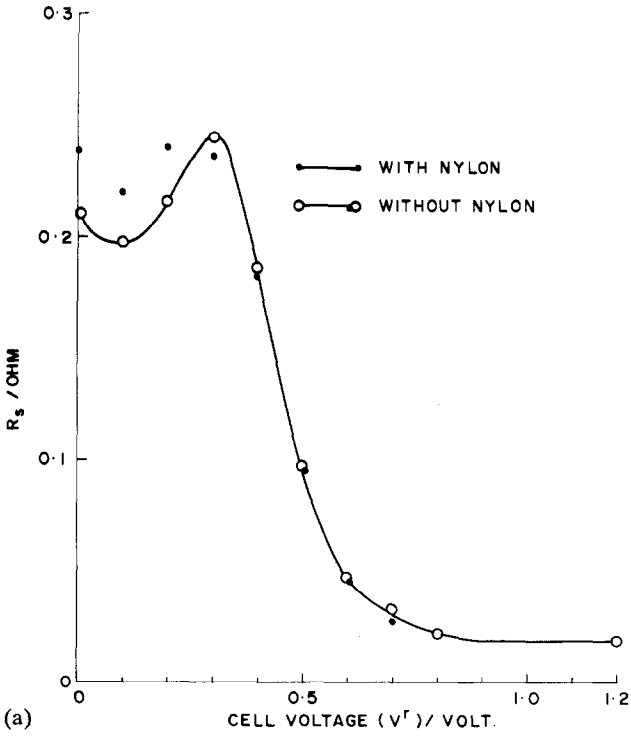


Fig. 1. Variation of (a) R_s and (b) $-X_s$ with cell voltage at 1 Hz with and without nylon hydrolysate.

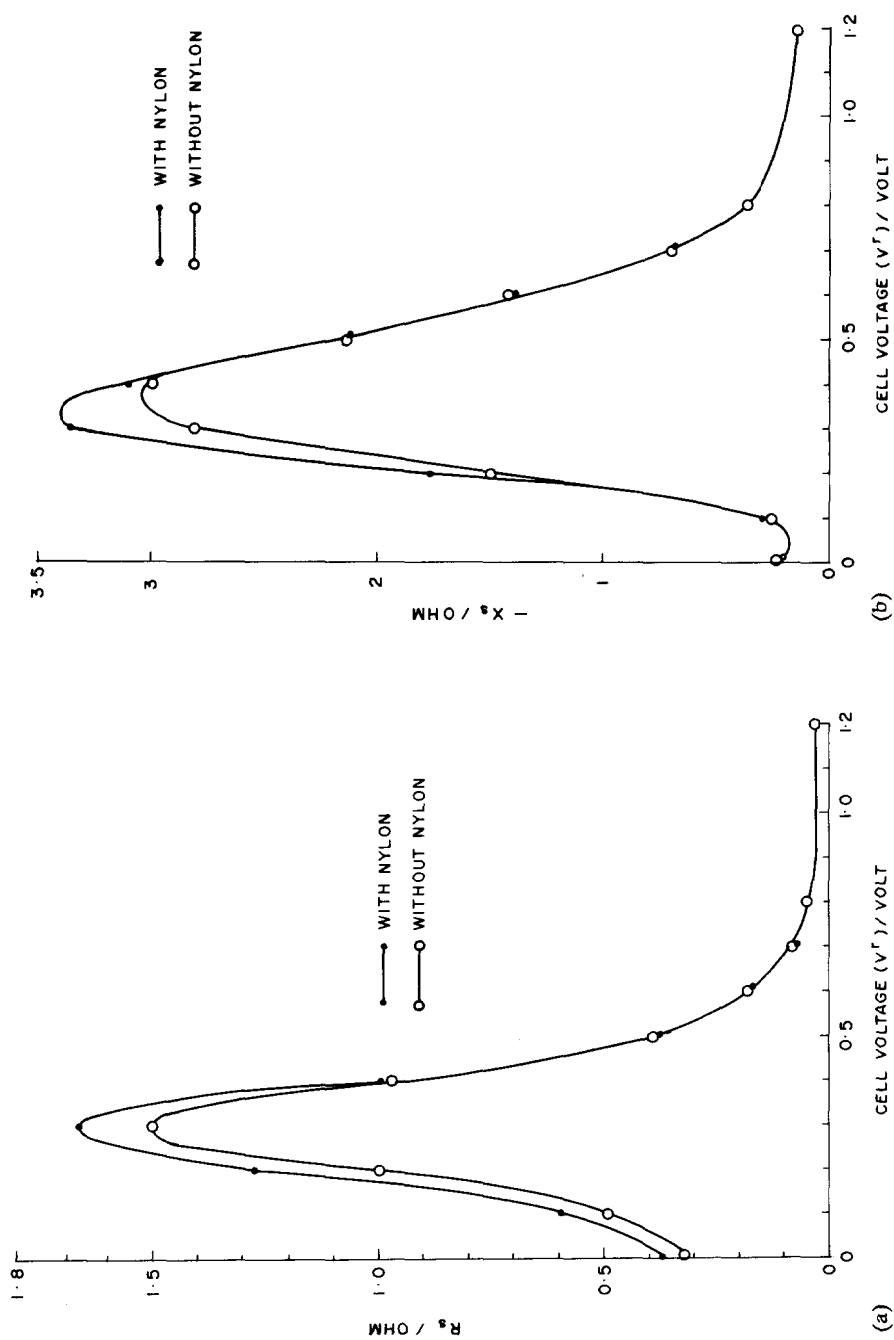


Fig. 2. Variation of (a) R_s and (b) $-X_s$ with cell voltage at 0.1 Hz with and without nylon hydrolysate.

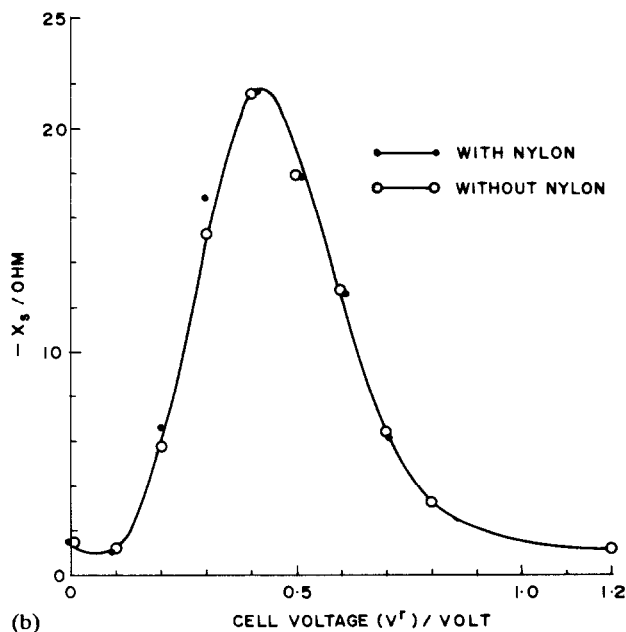
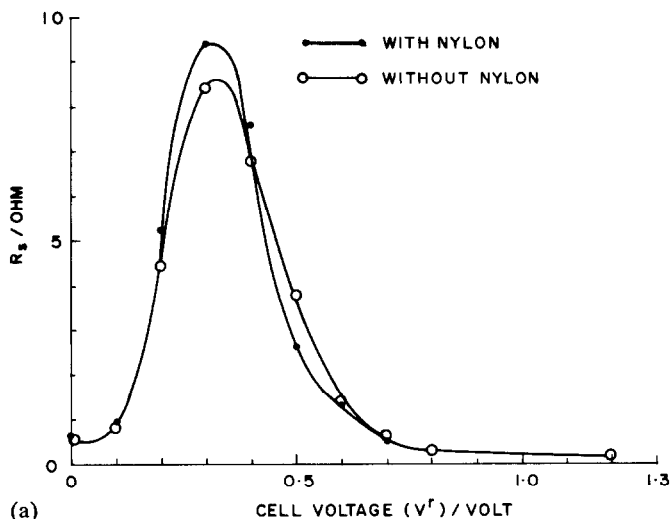


Fig. 3. Variation of (a) R_s and (b) $-X_s$ with cell voltage at 0.01 Hz with and without nylon hydrolysate.

The complex plane plots of the cell impedance at 0.3 and 0.4 V are shown in Figs. 4 and 5, respectively. Around this cell voltage, the potential of the nickel oxide electrode is far away from that of the HER and Ni(II)/Ni(III) reactions. Hence, the impedance of the cell is due to the double-layer at the nickel oxide electrode [2].

For the nickel electrode, the potential of zero charge is 0.4 to 0.5 V versus a Cd/Cd(OH)₂ reference electrode [4]. Hence, adsorption of neutral organic molecules

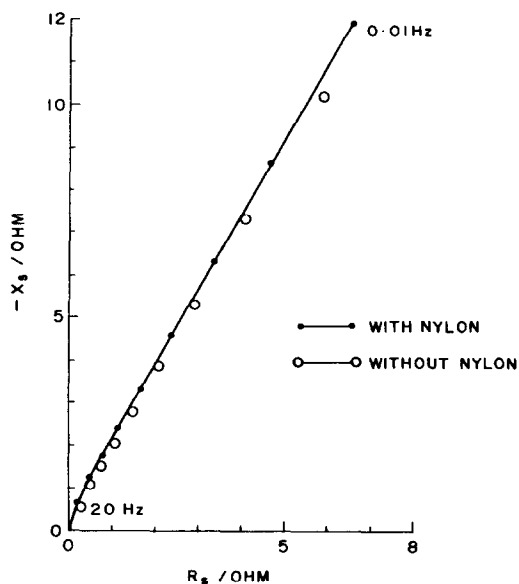


Fig. 4. Complex plane plot of cell impedance at voltage of 0.3 V with and without nylon hydrolysate.

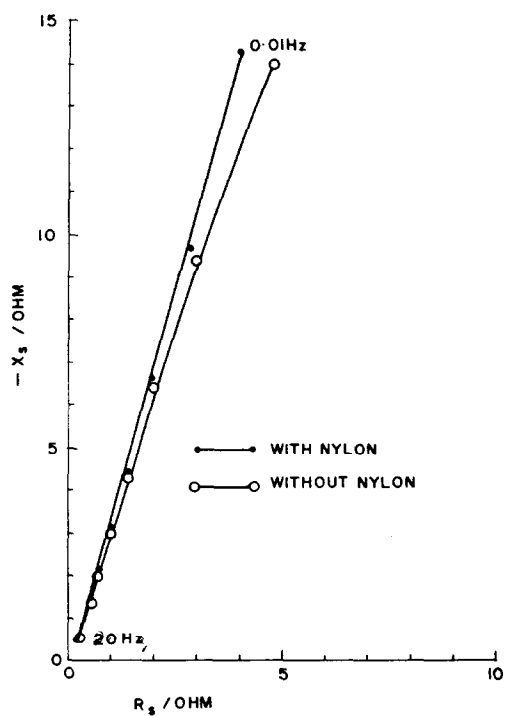


Fig. 5. Complex plane plot of cell impedance at voltage of 0.4 V with and without nylon hydrolysate.

is expected around this voltage. If such an adsorption does occur, it should alter the capacitive reactance of the double-layer around 0.4 V. The data in Figs. 4 and 5 show that nylon hydrolysate exerts only a slight effect on the impedance spectrum.

At a voltage of 0.0 V in a positive limited nickel/cadmium cell, the impedance is due to the HER at the nickel oxide electrode [2]. The impedance spectrum of the cell at 0.0 V is plotted in Fig. 6. It can be seen that the slope of the linear region is not affected by the presence of nylon hydrolysate. There is a slight shift along the R_s -axis; this indicates an increase in the charge-transfer resistance (R_{ct}) due to nylon hydrolysate.

The impedance of the cell was expected to be affected by presence of nylon hydrolysate, particularly around 0.4 V. Even though there is a slight change in the cell impedance due to nylon hydrolysate, specific signatures of the presence of hydrolysate are not seen. The changes observed could well be due to other reasons. The separation of the cause and the effect is not possible. Beyond 0.7 V, where the Ni(II)/Ni(III) reaction dominates, nylon is not expected to have a major influence on the impedance for the following reasons:

- (i) the reaction is a solid-state reaction and the rate-limiting factor is the diffusion within the solid state;
- (ii) the potential is well away from the potential of zero charge of the nickel electrode, and
- (iii) the exchange current of the Ni(II)/Ni(III) reaction is very large.

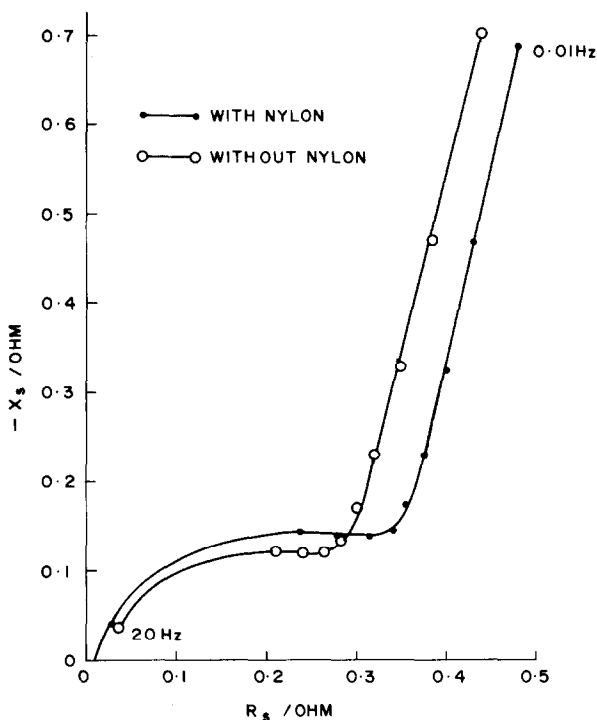


Fig. 6. Complex plane plot of cell impedance at voltage of 0.0 V with and without nylon hydrolysate.

Conclusions

Impedance measurements are generally believed to reveal degradation in nickel/cadmium and other cells. This study shows that cell impedance does not yield much information about nylon hydrolysis in nickel/cadmium cells. While minor changes are observed, they are not of sufficient significance to be treated as signatures of nylon hydrolysis.

Acknowledgements

The author is grateful to the Director, ISRO Satellite Centre, Bangalore for permission to publish this work. Thanks are to Mr P. Ramachandran, Deputy Director, ISRO Satellite Centre, Mr B.L. Agrawal, Group Director, Power Systems Group and Dr A. Subrahmanyam, Head, Batteries Division for permission to perform this work. Author is indebted to late Professor S. Sathyanarayana for his guidance.

References

- 1 W.R. Scott and D.W. Rusta, Sealed cell nickel-cadmium application manual, *NASA RP 1052*, 1979.
- 2 M.S. Suresh and S. Sathyanarayana, *J. Power Sources*, 37 (1992) 335-345.
- 3 S.U. Falk and A.J. Alkind, *Alkaline Storage Batteries*, Wiley, New York, 1969.
- 4 J.O'M. Bockris and A.K. N. Reddy, *Modern Aspects of Electrochemistry*, Vol. 2, Plenum, New York, 1970, p. 1246.