

Raman spectral observation of a 'new phase' observed in nickel electrodes cycled to failure

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Abstract

A 'new phase' is reported in nickel electrodes from Ni-H₂ boilerplate cells which were cycled to failure in electrolyte of variable KOH concentration (21-36%). Raman spectra clearly show the presence of this phase, and these spectra have been used to estimate the amounts present on these electrodes. Ten of twelve electrodes examined contain this new phase. The cycle life at higher KOH concentrations (31 and 36%) was greatly reduced, and nickel electrodes from these cells exhibited extensive amounts of this new phase. The presence of this 'new phase' correlates with cell failure defined by low end of discharge voltages. It is proposed that the lowered capacity and failure of these electrodes was caused by loss of active mass and formation of a phase with reduced electrochemical activity. These results indicate that formation of this new phase is accelerated at higher KOH concentrations.

Introduction

Ni-H₂ boilerplate cells containing 26% KOH displayed the longest cycle life in a recent study by Lim and Verzwylt [1]. Electrodes were cycled to failure in electrolyte of variable KOH concentration (21-36% KOH), at 80% depth of discharge in an accelerated cycle regime (6.24 A h nominal capacity). The cycle life of the 26% KOH cells was nine times greater than the cycle life of the conventional 31% KOH cells.

The Raman spectra of electrodes from these cells have been studied to characterize the active mass structure, as well as any other phases that might be present. Observation of a second phase is important because such a phase can be detrimental, adversely influencing cycle life and contributing to failure. Raman spectra provide a signature which is characteristic of each solid phase (or compound) present [2]. Furthermore, each spectrum carries structural information about each phase.

In previous work, it has been shown that Raman spectra can be used to characterize the NiO₂ layer stacking in nickel hydroxides and oxyhydroxides

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as close packed (ABAB...) or non-close packed (ABBCCA...) [2, 3]. β -nickel hydroxides are close packed. Active mass, charged or discharged, is non-close packed. X-ray powder diffraction patterns and EXAFS spectra have been successfully interpreted using a non-close packed layer structure, supporting this structural conclusion [3, 4]. Raman spectroscopy also allows structural differentiation of precursor materials and 'formed' active mass [2]. The precursor structure with cobalt differs from the precursor structure without cobalt.

Experimental

Raman spectra discussed herein are *ex situ* scans of electrodes which were removed from the cells in the discharged state. Spectra have been collected for both the front (non-screen side) and the back (screen side) of sectors taken from these electrodes. Two electrodes were studied from each cell (position 1, top; position 6, bottom of cell stack). The electrode ID numbers, KOH concentrations and cycle lives are given in Table 1 [1]. The 26% KOH cell containing electrodes 21-05 and 03-02 was removed from cycling before failure. A low end of discharge voltage (EODV) accounted for failure of the 31 and 36% KOH cells. The remaining cells ($\leq 26\%$ KOH) failed by a soft short.

TABLE 1

Quantitative determination of 'new-phase' content (%X) for Hughes electrodes with variable KOH concentration, using Raman spectral analysis

ID	%KOH	Position	No. of cycles [1] ^a	Side		Average (%X)	
				Front (non-screen) (%X)	Back (screen) (%X)	of 4	of 8
27-03	36	1	1845/1268	49	63	44	56
35-09	36	6		62	0		
25-09	31	1	3275/2979	71	0	68	29
27-07	31	6		100	100		
20-01	26	1	> 39 573/39 230	52	0	33	23
19-06	26	6		80	0		
21-05	26	1	> 30 549/> 30 549	27	0	24	
03-02	26	6		69	0		
04-03	23.5	1	> 28 495/4803	100	0	46	
16-09	23.5	6		85	0		
28-05	21	1	> 38 191/5047	0	0	0	
24-01	21	6		0	0		
08-09				0	0		

^aNo. of cycles to 0.5 V EODV/no. of cycles to 0.9 V EODV.

The Raman instrumentation and scan conditions have been previously described [2]. The compositions (wt.% 'new phase') have been estimated from the relative peak intensities (I_{553} versus I_{470} ratio), using a technique developed previously for quantitative analysis of coal dust–diesel particulate mixtures [5]. Material at or near the surface (in the volume illuminated and sampled by the laser beam) is measured. Material that is deeper within the electrode is not sampled. The compositions for the volumes sampled are believed to be representative, as an approximate measure of the amount of new phase.

Results and discussion

A Raman spectrum was scanned of each face of the 12 electrodes. Most spectra exhibit the expected doublet spectrum of discharged active mass (Fig. 1(a)) [2]. A four-peak spectral signature, which has not previously been documented, is observed in spectra scanned on 12 of 24 electrode faces (Table 1). This spectrum is characteristic of the presence of an additional phase, a phase not previously reported. A spectrum of an electrode displaying a predominant amount of this new phase is shown in Fig. 1(b). This 'new phase' shall be referred to hereafter as 'phase-X'.

Ten of the twelve electrodes studied contain phase-X (Table 1). Two of these show phase-X on both sides. In general, the front side exhibited the larger amount of phase-X. The front side faces the KOH and hydrogen electrode. The fact that the unused electrode (no. 08-09) showed no phase-X suggests that phase-X is produced during cycling in KOH electrolyte.

To facilitate electrode comparison, average compositions are given in Table 1, averaging over eight sides (for four electrodes) and over four sides (for two electrodes). The 31% and 36% KOH electrodes contain extensive amounts of phase-X on the average (56% average, over 8 electrode sides), and on both the front and back sides. By comparison, the 26% KOH electrodes display both a lower average (29%) and lower absolute percentages of phase-X.

First, the 26% KOH samples will be compared with the higher percent KOH samples (31% and 36% KOH). The high-KOH samples exhibited lower cycle life and more phase-X. The failure mode for these 4 high-KOH electrodes was a low end of discharge voltage (EODV) at low cycle life (<4000 cycles using either the 0.9 or 0.5 V EODV criterion) [1]. The observation that these electrodes display the most phase-X suggests that the phase-X may be instrumental in reducing cycle life, perhaps by inducing the low EODV. Also, a KOH concentration dependence is implied, with the 31% and 36% KOH concentrations favoring phase-X formation.

Phase-X is displayed on only one side, the front, of the lower KOH electrodes (<26% KOH). These electrodes all cycled to greater than 28 000 cycles with the 0.5 EODV criterion [1]. Except for the cell removed before

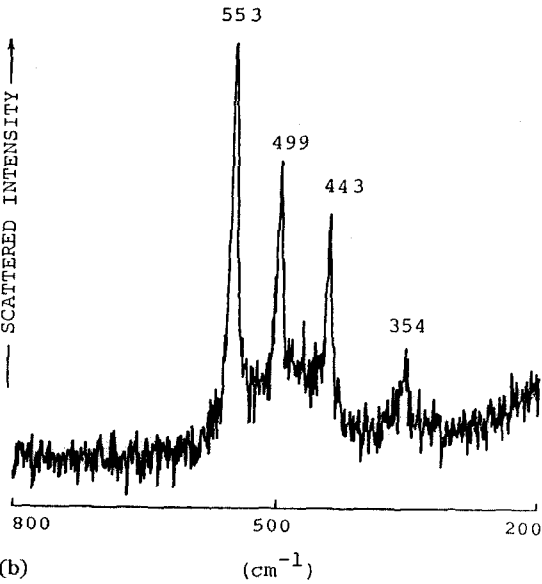
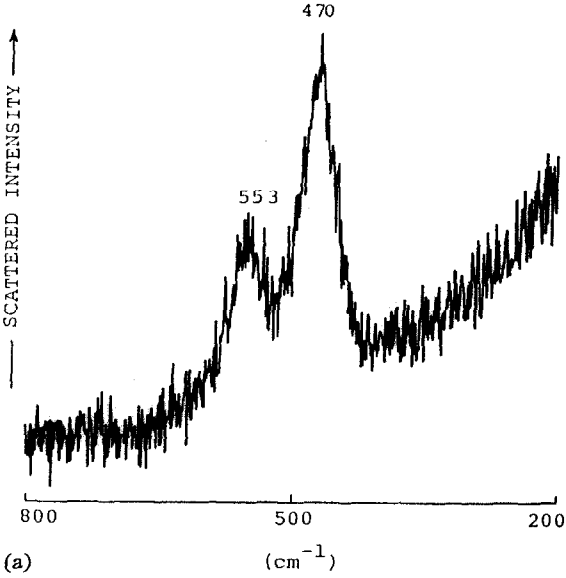


Fig. 1. Raman spectra of: (a) discharged active mass (ID no. 16-09); (b) 'phase-X (ID no. 04-03)'.

failure, they all failed due to a soft short. When phase-X is *not* formed on both sides of the electrode, it appears to have a less detrimental effect on cycle life, and a low EODV is not induced. This observation suggests

phase-X is first formed on the front of the electrode. If formation begins on the front side and propagates through to the back side, observation on both sides indicates that much more phase-X is present, throughout the electrode. Therefore, observation of phase-X on both sides of the 31 and 36% KOH electrodes is indicative of a much more extensive formation of phase-X. This is consistent with the greatly reduced cycle lives.

A KOH concentration dependence is implied, with higher KOH concentrations favoring phase-X formation. The 26% KOH electrodes all have a lower amount of phase-X than the 31% and 36% KOH electrodes. The 21% KOH electrodes exhibit no phase-X on either side. The 23.5% KOH electrodes appear to break this trend. The 23.5% KOH electrodes display more phase-X on the front side than the 26% KOH electrodes. However, the semi-quantitative nature of these values suggests these numbers may not differ significantly. That is, the 46% phase-X value (average of 4) for the 23.5% KOH is not that much greater than the 33% phase-X value for the first 26% KOH cell (and is less than the 56% phase-X value (average of 8) for the 31 and 36% KOH cells). This is especially true in light of the fact that the phase-X is only observed on one side for the 23.5 and 26% KOH electrodes, and the amounts on the interior are not estimated. Therefore, the amount of phase-X increase can be taken in the order: 21% < 23.5% \approx 26% < 31% \approx 36% KOH. We, therefore, propose that the higher KOH concentrations favor and accelerate phase-X formation.

Phase-X is not simply induced by extensive cycling, because it is clear that the phase-X content does not correlate with *high* cycle life. Electrodes with 31% and 36% KOH, with the most phase-X, show the lowest cycle life. The phase-X content is lower in the 26% KOH electrodes, which display the longest cycle life. The 21% KOH electrodes were cycled extensively, but display no phase-X.

Furthermore, since 21% and 23.5% KOH electrodes have drastically different amounts of phase-X, it appears that phase-X does not account for the secondary plateau formation reported below 26% KOH by Lim and Verzwylt [1].

The fact that the front of the electrode (which is closer to the counter electrode) has more phase-X than the back is consistent with greater utilization of the active mass on the side facing the hydrogen electrode and separator containing KOH. This front of the nickel electrode is directly exposed to KOH. This exposure as well as differences in current densities and voltage drops between the front and the back side of an electrode may be factors influencing phase-X formation.

Conclusions

The presence of phase-X is correlated with cell failure at high KOH concentration (31–36%) due to a low end of discharge voltage. That is, these electrodes display a reduced capacity at low cycle life. It is proposed that

this lowered capacity is caused by a phase transformation from active mass to a phase which is less electrochemically active, thereby reducing electrode utilization. It is apparent that higher KOH concentrations favor formation of this new phase.

These results suggest that avoidance of the soft short failure mechanism, observed for <26% KOH electrodes, might allow even greater electrode cycle life for the KOH concentrations below 26% KOH. It becomes obvious that the apparent maximum performance at 26% KOH is controlled by multiple failure modes, not only phase-X formation.

It has often been proposed that a 'less active phase' may be formed and may be detrimental to the electrochemical behavior of the nickel electrode. This is, to our knowledge, the first time that this phase has been directly observed in active mass. The structural identification of this phase is in progress.

Acknowledgement

Support by NASA, Lewis Research Center under Grant No. NAG3-519 is gratefully acknowledged.

References

- 1 H. S. Lim and S. A. Verzwylvelt, *J. Power Sources*, 29 (1990) 503-519.
- 2 B. C. Cornilsen, X. Shan and P. L. Loyselle, *J. Power Sources*, 29 (1990) 453-466.
- 3 B. C. Cornilsen, P. J. Karjala and P. L. Loyselle, *J. Power Sources*, 22 (1988) 351-357.
- 4 B. C. Cornilsen, X. Shan and P. L. Loyselle, in D. Corrigan and A. Zimmerman (eds.), *Nickel Hydroxide Electrodes*, Vol. 90-4, The Electrochemical Society, Pennington, NJ, 1990, pp. 82-96.
- 5 B. C. Cornilsen, J. H. Johnson, P. L. Loyselle and D. H. Carlson, in R. E. Glenn (ed.), *Proc. VIIth Int. Pneumoconioses Conf., DHHS (NIOSH) Publication No. 90-108, Part 1*, U.S. Dept. of Health and Human Services, NIOSH, Pittsburgh, PA, 1990, pp. 656-662.