GAS PHASE INVESTIGATIONS OF NICKEL-METALHYDRIDE BATTERIES

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Abstract: This paper reports on in-line analysis of gas production in rechargeable batteries. Raman spectroscopy was used to study the effects of (over-) charging and discharging. In this way the contribution of oxygen, hydrogen and nitrogen can be estimated, where before only total pressure information was available.

The rechargeable sealed Nickel-MetalHydride (Ni-MH) battery is one of the latest developments in battery technologies. Its main advantages are environmental friendliness and high energy density. The control of the internal pressure in these sealed rechargeable NiMH batteries is very critical. The design of the battery allows an increase in pressure up to 15 bars. This pressure increase is related to the high gas generation rate, especially during extreme operating conditions, like overcharge and overdischarge.

During battery operation the main reactions, occurring at the Ni and the MH electrode can be represented by:

$$x\ Ni(OH)_2 + x\ OH^- \leftrightarrow x\ NiOOH + x\ H_2O + x\ e^- \quad (1)$$

$$M + x\ H_2O + x\ e^- \leftrightarrow MH_x + x\ OH^- \quad (2)$$

In addition to the above main storage reactions, side reactions lead to O_2 and H_2 generation during overcharging at the Ni and MH electrode, respectively. The generated oxygen gas normally recombines at the MH electrode. To investigate the kinetics of both gas generation and recombination, information about the gas phase composition during different operating conditions is very important. Raman spectroscopy was selected as analysing tool, which allows *in-situ* analyses of the gas composition during battery operation.

Fig. 1 shows a typical analysis, where the battery potential and the composition of the gases, represented in terms of partial pressures, are plotted against time.

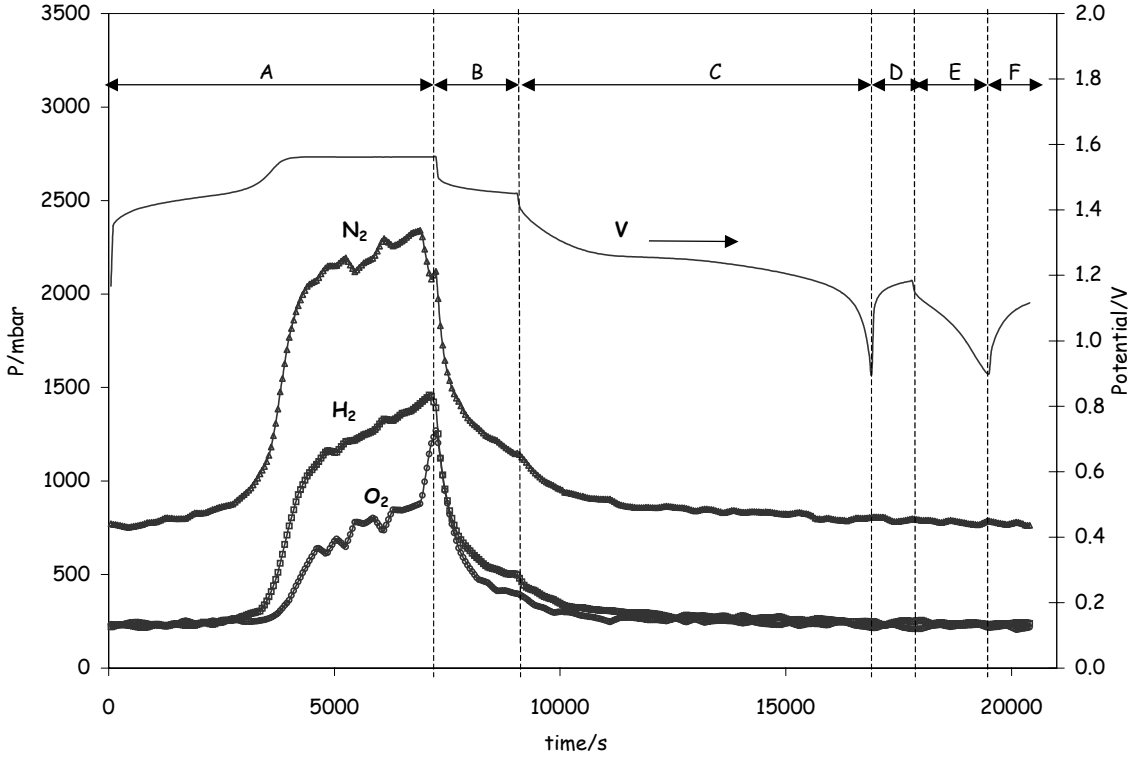

Fig. 1. Gas composition inside a Ni-MH battery. A: Battery charged to 100% overcharge at 1C-rate; B: Rest (I=0) for 30 min; C: Discharge at 0.5 C-rate till 0.9V; D and F: Rest for 15 min; E: Discharge at 0.1C-rate till 0.9V. C-rate = I_{charge} [A]/Capacity [Ah].

Charging cycles like the one shown in Fig. 1 are studied for periods as long as a week. This means that special attention needs to be paid to calibration during the analysis.

Qualitative and quantitative Raman spectroscopic analyses of the gas phase during sealed battery operation were successfully achieved. Three gases were analysed: O_2, H_2 and N_2. The relative importance of H_2 compared to O_2 depends on the current imposed to the battery and on the temperature. When the battery temperature is kept constant at 25°C, the O_2 concentration was found to be dominant at low charging current (<0.5A), while the opposite is true at high currents (>1A). Nitrogen concentration is found to change also during charging despite its assumed inertness. It was shown by mass spectroscopic analyses that this concentration change could be linked to changes of the internal volume of the electrodes and electrolyte.

With the above results new battery models can be developed that can help in creating safer batteries that can be charged at high speeds.