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Pseudo Resistance Curves for Aluminium Cell Control - Alumina Dissolution and Cell Dynamics

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Abstract

The pseudo resistance was measured as a function of the alumina concentration in the bath in five different types of cells. The pseudo resistance showed a minimum value at 5.0 to 5.5 mass% Al_2O_3, when the bath samples were analyzed by the LECO method. To the left of the minimum point on the curve the slope increased gradually until the anode effect occurred at 1.6 to 2.2 mass% Al_2O_3, while a nearly linear curve was found in some of the measurements. The difference in pseudo resistance determined just prior to the anode effect and at the minimum point, corresponded to a voltage difference between 100 and 300 mV. Immediately after the alumina feeding rate was reduced from overfeeding to underfeeding, a so-called "hysteresis effect" could be observed. This was characterized by a sudden decrease in cell voltage of about 100 mV in less than 30 minutes, in spite of practically constant bath composition and temperature in this time period. This effect may be caused by dissolution of alumina sludge in the bath phase above the metal pad, accumulated during the long overfeeding period of several hours, which was necessary to reach alumina concentrations to the right of the minimum point on the curve.

Introduction

Process control in industrial aluminium electrolysis cells could in principle consist of following the change in cell voltage in response to alumina feeding and changing interpolar distance. However, cell voltage is seldom used for cell control because small fluctuations in line current, as commonly occur, cause variations in cell voltage not related to changes in alumina concentration in the bath or interpolar distance (1).

Hence, a pseudo resistance, R_p, given in micro ohm, is used, where:

$$R_p = (V - V_{ext}) / I \qquad (1)$$

Here, V is the measured cell voltage in volts,
I is the line current in ampères,
V_{ext} is the zero current intercept of V versus I for small changes in current.

Because R_p is not altered by small fluctuations in line current, it gives a much more stable signal for the computer than the cell voltage. Subtraction of a constant from the cell voltage and division by the line current do not alter the shape of the curve for voltage as a function of alumina concentration. Thus, the curve for the pseudo resistance as a function of alumina concentration will have the same shape as for the cell voltage.

V_{ext} is sometimes erroneously referred to as the counter electromotive force, or back emf of the cell. Actually, V_{ext} has no thermodynamic significance. It usually ranges between 1.62 V and 1.68 V, depending upon several parameters, including alumina concentration (2). V_{ext} is usually taken as a constant, and in our case we have chosen 1.7 V, for pseudo resistance control. A small error in this value has little effect on the electrical noise generated by line current variations.

Pseudo resistance as a function of alumina concentration in the bath is now commonly used for cell control. Pseudo resistance curves can be calculated theoretically, see e.g., Kvande et al. (1). Apparently, there have been published very few experimental curves from industrial cells. The only measured data we have found in the literature, are those given by Welch (2) and Li et al. (3).

It is the main purpose of the present paper to discuss measured pseudo resistance curves from various types of cells. Several questions now remain unanswered. Does the shape of these curves agree with theoretical calculations? Are the curves cell dependent? Are they dependent on the experimental conditions, for example the rate of change in alumina concentration with time (percentage of overfeeding or underfeeding)? At what alumina concentration does the minimum pseudo resistance occur? And finally, what is the difference in pseudo resistance measured just prior to the occurrence of an anode effect and at the minimum point on the curve?

The answers to these questions may give valuable additional information about the cell control strategy that has been chosen. The question of the optimum alumina concentration in the bath may be discussed on the basis of the present measurements. The target is then mainly to minimize energy consumption and to maximize current efficiency.

Theory

Cell voltage can be broken down into several components, that consist of both non-ohmic polarization voltage terms and ohmic voltages. A detailed description has been given by Haupin (4), and the equations will not be repeated here.

According to Holmes (5), in the mid 1960s the pre-anode effect rise in cell voltage and resistance could be measured with the introduction of the first process control computers and automatic point feeders for alumina. At the same time Welch (6) was probably the first to publish theoretical curves for the change in cell voltage as a function of alumina concentration in the bath for different anode current densities. These curves are now the basis of all process control strategies for modern cells.

Experimental

Bath Sampling. Before bath samples were taken, an opening in the top crust was made at a suitable position in the cell, usually in the tapping hole for side-by-side cells, or near the centre of the longitudinal side for end-to-end cells. In the latter case an iron tube with a removable lid was frozen into the crust around the hole to prevent any alumina powder from contaminating the bath samples. Careful bath sampling is of crucial importance in these types of measurements. It is assumed that any alumina concentration gradients in the bath would be negligible in this case. Control bath samples taken at the duct end and at other positions in side-by-side cells gave identical values to those from the tap end.

Bath samples were taken by simply dipping a steel rod (diameter 10 or 20 mm) about 5 to 10 cm into the bath and removing it after 1 to 2 seconds. The amount of solidified bath on the steel rod was then sufficient to provide a bath sample for alumina analysis. Larger samples taken by a bath tong gave similar results. Samples were also taken occasionally for analyses of the AlF_3 and CaF_2 contents by an X-ray method. Bath temperatures were measured regularly by use of a standard thermocouple.

Bath Analysis. The bath samples were analysed with respect to the alumina content by the LECO method. The LECO apparatus was of the type RO-336, and the analyses were performed at SINTEF in Trondheim, Norway. The uncertainty in the alumina content determined by the LECO analysis is given as less than ± 5% (relative). These data then gave the alumina concentration as a function of time at various feeding rates.

Procedure. At the beginning of each measurement series, the anode regulation was set in manual to avoid any automatic regulations during the test period. The selected rate of overfeeding or underfeeding was adjusted and kept constant through data communication with the computer. Major cell operational disturbances, like anode changing, metal tapping and anode beam raising, were avoided during the bath sampling period. Bath and metal heights were measured, but showed no variation within the precision of the measurements.

Data for the pseudo resistance of the cell were logged continuously and averaged over five-minute periods. The values of pseudo resistance versus time were later correlated with the corresponding alumina concentrations to construct pseudo resistance curves.

Most of the experiments were carried out as follows:

- Overfeeding (120-180% of the theoretical consumption) for variable lengths of time and variable alumina concentrations, followed by:

- Underfeeding (0-70% of the theoretical consumption) until or just prior to an anode effect.

Cell Dynamics. The pseudo resistance curves shown in the present paper were found by transient procedures, and the dynamic impact of changing bath temperature, side ledge freezing or melting, and sludge accumulation or dissolution, may all influence the curves for pseudo resistance as a function of alumina concentration to a variable degree. In an attempt to describe any deviations from the theoretical stationary pseudo resistance curve, dynamic models of the cells were employed, with transient predictions of cell resistance, energy balance and alumina dissolution.

Results

Alumina content versus time. In the large majority of the measurements the alumina content showed a linear dependence with time, even for overfeeding periods of up to 6 hours. An example is shown in Fig. 1. In a few cases the increase in alumina content with time levelled off at high values (6 to 7 mass% Al_2O_3), which is close to the solubility limit of 7.5 to 8.0 mass% for these bath compositions and temperatures (7, 8).

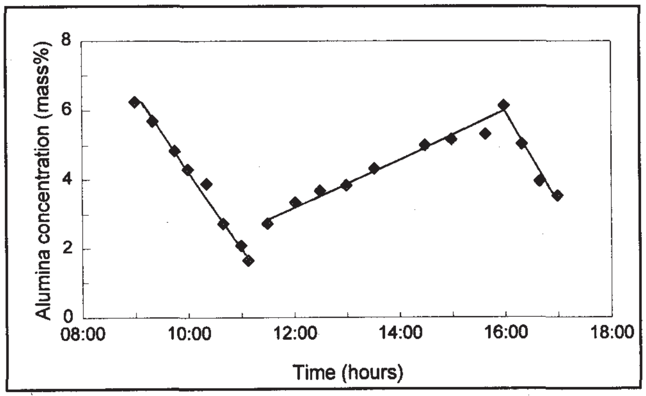

Figure 1: Examples of measured alumina concentrations as a function of time for two periods with no alumina feeding and for one overfeeding period (135%) for a 175 kA prebake cell.

Change in alumina content versus percentage of overfeeding or underfeeding. Such curves were also drawn on the basis of the LECO analyses, see Fig. 2. The slope could be used to obtain an approximate calculation of the amount of molten bath present in the cell, from the given line amperage and an estimated value for the current efficiency.

Pseudo resistance curves. These curves are the main results from the measurements, and their interpretation may give answers to the questions in the "Introduction" section of the present paper. Altogether we have now done about 25 series of measurements in five different types of cells, including Söderberg cells. Here we will select a few examples for illustration of the results obtained, and particularly study the shape of the different pseudo resistance curves. The main features of these curves will then be described and discussed.

Figs. 3 and 4 show examples of results for the same cell, but measured about one month apart. The curves are similar, but they also show some differences.

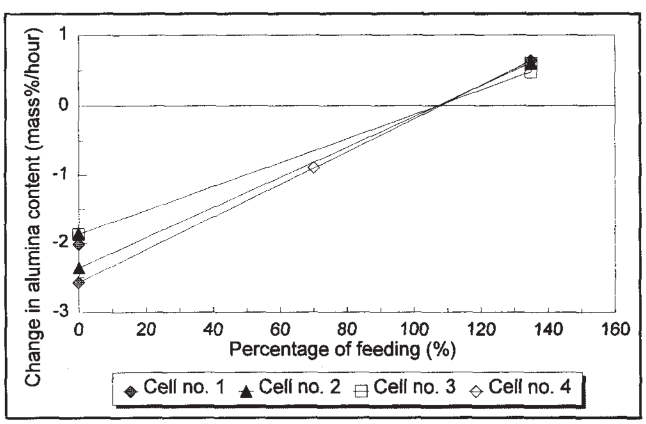

Figure 2: Changes in alumina content vs. percentage of feeding for four 175 kA prebake cells.

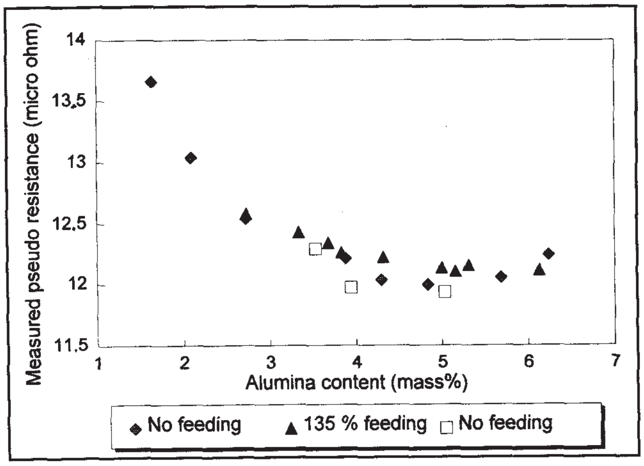

Figure 3: Pseudo resistance curves for a 175 kA prebake cell.

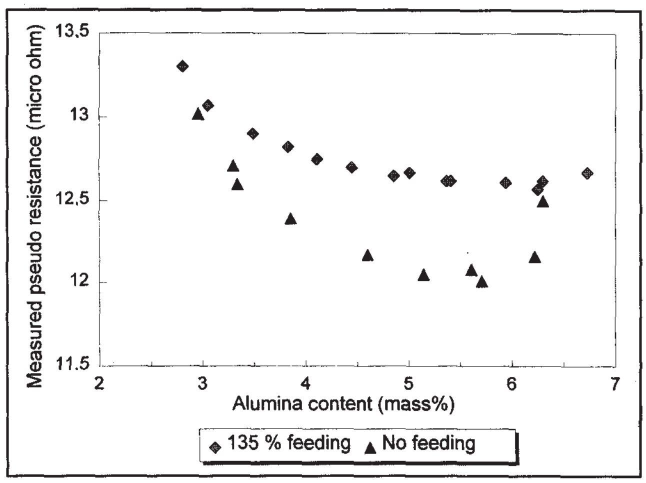

Figure 4: Pseudo resistance curves for a 175 kA prebake cell (the same cell as in Figure 3, but measured one month later).

Generally, the following conclusions may be drawn from the present measurements:

1. The minimum value of the pseudo resistance occurred for alumina concentrations at 5.0 to 5.5 mass% Al_2O_3. This minimum appeared to be roughly independent of overfeeding or underfeeding conditions, and also of the cell size and design.

2. Anode effects were found to occur at alumina concentrations in the range from 1.6 to 2.2 mass%.

3. The difference in pseudo resistance between measurements made at (or just prior to) the anode effect and at the minimum point, corresponded to a voltage difference in the range from 100 to 300 mV.

4. The curves were dependent on the rate of alumina feeding. When underfeeding was started after a period of overfeeding, the pseudo resistance then dropped rapidly, even if both the alumina content and the bath temperature remained approximately constant. This behaviour was at first somewhat surprising. In lack of a better description we have chosen to call this a "hysteresis effect". It is an interesting observation, which so far has not been reported in the literature or included in the theoretical calculations. This will be discussed below.

Discussion

Minimum on the pseudo resistance curve

The alumina content at the minimum point on the pseudo resistance curve appeared to be independent of the experimental conditions, i.e., the degree of overfeeding or underfeeding. If we take the average value from 14 series of measurements in four different types of prebaked cells in the amperage range of 170 to 230 kA, we find that the minimum point is at (5.3 ± 0.2) mass% Al_2O_3. The uncertainty is here taken as the standard deviation in the average value of these 14 sets of data. This is in good agreement with the early calculations by Welch (6), but it is significantly higher than the data from a later work by the same author (2), who reported both theoretical and experimental minimum values at about 3.5 mass% Al_2O_3. More recent theoretical calculations by Kvande et al. (1) indicated a minimum point at 4.2 to 4.3 mass%. Thus, the present high value indicates that the latter theoretical model (1) may not describe the experimental results adequately, and that a theoretical refinement of the model is necessary.

Curvature of the pseudo resistance curves

Theoretically, these curves should have a gradually increasing (more negative) slope for decreasing alumina concentration until the anode effect occurs. In practice we observed this increasing curvature in about half of our measurements, while the other half showed a nearly linear curve with decreasing alumina content. This may be related to the experimental conditions, particularly the rate of alumina feeding and sludge formation and dissolution. Measurements in the same type of cell could give either increasing or constant slope on the left-hand side of the pseudo resistance curve.

During underfeeding periods some of the sludge present underneath the metal pad is removed and dissolved in the bath. When this happens, the apparent metal height decreases, and the interpolar distance and the pseudo resistance should therefore increase, as the anode beam position was kept constant during the measurements. Contrary to this, lower pseudo resistances were found in underfeeding periods, however.

The bath temperature increased significantly with decreasing alumina concentration (underfeeding). The difference in temperature between the minimum point on the curve and some point close to the anode effect was measured to be 10 to 20 °C. Literature data (9) show that the effect of this temperature change on the electrical conductivity of the bath is small compared to the influence of the alumina content. Thus, the temperature effect alone cannot explain the observed changes in pseudo resistance.

The "hysteresis effect"

As mentioned already, we observed that the pseudo resistance was higher when measured during overfeeding of alumina compared to underfeeding for a given alumina content in the bath. In order to try to quantify this we may define a "hysteresis effect" as the maximum reduction in pseudo resistance (or cell voltage) at constant alumina concentration after the change from overfeeding to underfeeding. The average value from about 10 series of measurements for one cell type was about 0.5 micro ohm, which corresponded to about 80 mV reduction in cell voltage. The "hysteresis effect" in Fig. 4 was 110 mV, while in other cases, for example in Fig. 3, it was only about 20 mV.

Another example is shown in Fig. 5, where the "hysteresis effect" again was about 100 mV (in 20 minutes), when the feeding was stopped after 6 hours of 130% alumina feeding. In this case the overfeeding and underfeeding curves were actually located at two rather different resistance levels, corresponding to a voltage difference of about 100 mV.

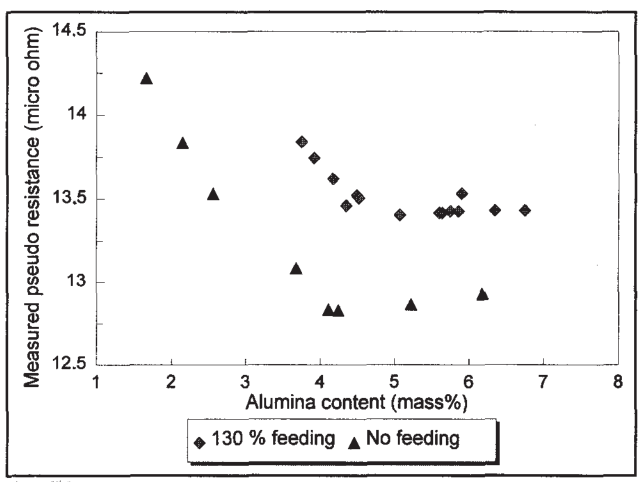

Figure 5: Pseudo resistance curves for a 175 kA prebake cell, showing a large "hysteresis effect".

In order to study this effect further, we took a closer look at the parameters that had been varied during the different measurement series. Qualitatively, the "hysteresis effect" was found to increase with increasing alumina content in the bath, as measured at the time of change from overfeeding to underfeeding. Furthermore, it was found to increase with decreasing average superheat, which is defined as the difference between the bath temperature and the corresponding liquidus temperature for the given bath composition. On the other hand, we could not find any significant correlation with the percentage of overfeeding in these experiments.

Sludge formation in the bath phase, a possible explanation of the "hysteresis effect".

To form bottom sludge, undissolved alumina and frozen bath must overcome the interfacial tension at the bath-metal interface and sink through the metal. However, if the size and mass of the alumina agglomerations are sufficiently small, they may sink to the bath-metal interface and then accumulate there. The possibilities of sludge formation in the bath on top of the metal pad have been discussed by Thonstad and Liu (10) and Keller (11). However, to our knowledge there is no published experimental evidence for the existence of alumina sludge, or undissolved alumina, in the bath phase above the metal pad in industrial cells.

The rapid reduction in cell voltage and pseudo resistance almost immediately after changing from overfeeding to underfeeding, indicates a corresponding rapid change in the electrical resistance of the bath in the interpolar space. Bath composition and temperature were then practically constant, and no significant change in the interpolar distance could occur in this short time interval (about 0.5 hours). Thus, the most plausible explanation of the "hysteresis effect" may be related to undissolved alumina that had been accumulated in the bath above the metal surface during several hours of overfeeding. This is then readily available for dissolution once the overfeeding period is over, and its dissolution rate will be much faster during underfeeding.

The results shown in Fig. 1 are typical for this type of measurements, and they showed a linear dependence of the dissolved alumina concentration in the bath as a function of time. This indicates that the rate of sludge accumulation in overfeeding periods may be practically constant with time, within the uncertainty of the measurements.

In certain cases a thin layer of solid cryolite may freeze out on the bath/metal interface. This may occur if the temperature of the bath close to the interface becomes lower than the corresponding liquidus temperature, and may be seen from the phase diagram (9). This solid cryolite would cause an increase in the bath resistance. However, because the bath temperature and composition remained practically constant during the rapid cell voltage reduction, which occurred in 20 to 30 minutes, we consider this effect to be small compared to the influence of undissolved alumina present on the metal surface.

The "hysteresis effect" and the dynamic modelling of the experiments

The higher pseudo resistance during overfeeding compared to the pseudo resistance measured during underfeeding, was reproducible for the experiments reported so far. The results also showed that bath superheat and alumina concentration could either be influenced by alumina dissolution and sludging, or by the energy balance and changes in side ledge thickness. To investigate this we have carried out simulations using one of the dynamic cell models of Hydro Aluminium a.s, with variable alumina dissolution models incorporated in the total dynamic cell model. The following observations were made:

* Simulated changes in bath temperature agreed with the measurements.
* The transient changes in bath temperature could not explain the "hysteresis effect" in the pseudo resistance when going from overfeeding to underfeeding.
* Side ledge melting and freezing could not explain the "hysteresis effect ".
* The observed "hysteresis effect" could not be explained by delayed transport of sludge to and from the cell bottom underneath the metal pad, and the corresponding effects on interpolar distance and pseudo resistance.
* The "hysteresis effect" could apparently only be explained by introduction of an additional electrical resistance term in the bath, due to undissolved alumina accumulated in the interpolar gap during the overfeeding period. The favoured alumina dissolution model then predicted transient changes in alumina concentration and bath resistance in good agreement with the measurements. After changing from overfeeding to underfeeding the amount of sludge was gradually reduced, and the cell resistance was also reduced to coincide with the theoretical pseudo resistance curve after some time.
* We were able to predict the effect of both superheat and alumina concentration on the observed "hysteresis effect", from knowledge of factors affecting alumina dissolution available in the literature, i.e., combined heat and mass transport. The effects of superheat and alumina concentration on sludging are in agreement with a recent theoretical treatment by Sterten et al. (12).

Point feeding of alumina

Point feeding of alumina was first used for a whole line of cells by Alcoa in 1961 (5) and has now been installed in most, if not all modern reduction cells. A typical cell may have 2 to 5 point feeders, and about 1 kg of alumina is added in each dump. Walker et al. (13) have recently discussed design considerations for selecting the number of point feeders in modern cells. They concluded that one feeder would be required for every 25 to 50 kA of cell current. However, many industrial cells have fewer feeders than this, and in some cell designs there may be only one feeder for every 75 kA or so.

More interestingly, Walker et al. (13) showed that complete alumina dissolution upon addition is unlikely to be achieved with the point feeder designs installed in most modern cells. They estimated that alumina additions between 0.6 and 1.2 kg would cool the feed mixing zone in the bath to its liquidus temperature, and that slow dissolution of aggregate and possibly sludge formation could be expected if significantly larger amounts of alumina were added. One would expect that the same thing would happen if the time period between each alumina addition was reduced significantly, such as during overfeeding.

Furthermore, it is important that the feeder holes in the crust are kept open between each feeding. Dispersed alumina powder will dissolve more readily than pieces of alumina agglomerates or solid crust. Other problems such as buildup of frozen bath on the point feeder breakers should also be avoided.

Effect of alumina feeding rate

In order to study the effect of the feeding rate of alumina on the "hysteresis effect", we then chose feeding rates of 115% and 90%, which are closer to the theoretical (ideal) alumina consumption rate than in the measurements described earlier. Two interesting observations were then made. Firstly, we found no "hysteresis effect" in this case. Therefore, it is tempting to conclude that the feeding rate is a contributing factor, in spite of our earlier results obtained for higher overfeeding rates.

Secondly, the observed time dependence of the change in alumina content in the bath was somewhat different. During the first 5 hours of overfeeding at 115% the alumina content increased, as expected, by about 0.44 mass% Al_2O_3 per hour. However, for the next 1.5 hours of overfeeding, the alumina content remained constant, at about 4.5 mass% Al_2O_3. The bath then looked much more viscous and "sluggish". A possible explanation is that a significant sludge formation must have occurred in the bath toward the end of this extended overfeeding period, although the bath then was not saturated with alumina. In this case the accumulation and dissolution may have been so slow that no "hysteresis effect" could be observed.

This was confirmed by a slow reduction in alumina content of only -0.3 mass% Al_2O_3 per hour during the first 3.5 hours of the 90% feeding period. After that time it increased to -0.46 mass% per hour for the remaining 4 hours of underfeeding until the anode effect occurred (at 1.85 mass% Al_2O_3). Thus, in this case it may have taken about 3.5 hours to dissolve the amount of sludge or undissolved alumina that was formed in the bath phase during the 6.5 hours of 115% feeding rate.

Effect of alumina content on cell operational parameters

We will now use the measured pseudo resistance curves to evaluate the effect of increasing alumina content in the bath on cell operational parameters. If we assume that the average alumina content could be increased from for example 2.5 to 3.5 mass% Al_2O_3, the present data indicate a potential decrease in cell voltage by about 90 mV and a lower bath temperature by 4 °C. This temperature reduction will increase current efficiency by about 0.8%, if we neglect any specific effect of the alumina content itself on current efficiency. Combined with the above cell voltage reduction, this could reduce energy consumption by about 3%, which amounts to -0.4 kWh/kg Al for modern cells. These are small, but important improvements that are worth striving for, because of their significant economic implications.

Process control

Most cells are now operated and controlled to maintain alumina concentrations in the bath that are well on the left-hand side of the minimum on the pseudo resistance curve. The reason for this choice is that the response with respect to changing alumina content is then large and clear, and it is beneficial in order to minimize sludge formation.

If we assume that the effect of alumina content on current efficiency is negligible (1), it would then appear to be more important to control the alumina concentration towards the minimum cell voltage. This would mean an average alumina concentration of about 5 mass% Al_2O_3. However, cell control is then more difficult, and the risk of sludge formation is considerably higher. If the sludge problem was avoided and the heat balance of the cell could be maintained satisfactorily, voltage savings of about 150 to 200 mV may then be possible. Alternatively, the amperage may be increased by up to 4 or 5 % to compensate for the reduced heat input by the lower cell voltage.

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