EVIDENCE OF AGGLOMERATION AND SYNERESIS
IN REGULAR AND EXCESS HEAT CELLS IN WATER

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Abstract
Agglomeration and syneresis of colloids in electrochemical cells affect cell voltages when the agglomerate adheres to electrodes. Electrode gassing can dislodge agglomerates which move under thermophoretic forces to the cooler cell wall; once adhered to the wall they can change the thermal conductivity of that wall which changes the cell constant. Agglomerates on the electrodes and the cell wall may undergo syneresis which consists of shrinking and restructuring. This may be triggered by a change of cell current and produces either a more resistive layer on the electrodes or a little sediment in the cell. Such changes in resistance can alter resistive heating but do not lead to excess heat. Excess heat is reported here as a function of a nickel cathode: soft nickel failed to produce excess heat while three samples of treated nickel were more productive. A parallel is drawn between these results on nickel and results reported by others for the palladium heavy water system.

Background
Dilute colloids of silica, trace metals and likely some bacteria exist as charged particles of various shapes and sizes in solution. Control of such species is mandatory in the microcircuit, pharmaceutical and electroplating industries. In an electrochemical cell, charged silica particles migrate and may coat an electrode with a monolayer but will not agglomerate further unless metal ions are present. Then, agglomerates form on an electrode like a house of cards, except the agglomerates are held by the charges rather than gravity. Agglomeration by electrophoresis has been described by others1,2. When the current changes, the agglomerate may undergo a dramatic crystalline change called syneresis. This may be a catastrophic change as if someone shook the table under the house of cards. The resultant layer may be much less porous and even quite resistive to ion transport; or it may detach from the electrode and drift away.

The following series of experiments is presented as a preliminary demonstration of agglomeration and syneresis which affect electrode voltages and cell constants: and of excess heating in ordinary water which appears to be a function of the cathode metal. These two distinct entities are presented as they unfolded from experimental results.
Experiments in Pyrex

First, a simple experiment was performed to understand how colloids agglomerate by electrophoresis. Figure 1 shows the resultant anodic agglomerate using the spent sodium metasilicate solution with metal salts present that were left after producing a "chemical garden" with a commercial kit from a child's science store. Oxygen left the anode through long tentacles. X-ray diffraction revealed that only amorphous silica was present in the deposit without visible metal bands. When tri- or tetrabasic metals are present, the agglomerate may form on the cathode.

Silica deposits are less obvious in a nickel/ordinary water cell with about 100 ppm silica present. ICP Mass Spec analysis found that carbonate solution in a Pyrex cell normally contains 100 to 200 ppm silica. Experiments reported at Nagoya\(^3\) (using a Pyrex Dewar cell, 30 cm\(^2\) nickel foil cathode and platinum wire anode) showed 100% levels of excess heat and 50% changes in the cell heating constant. After two weeks of operation the stir bar ceased rotation. Front illumination of bubbles that clung to the stir bar revealed that the stuck bar was encased in a gel. Subsequently, simple Pyrex test tubes (in a constant temperature bath) were employed with stirring power improved by a closer drive magnet. In one Pyrex cell, the stirring bar became covered in gas bubbles which were not disturbed by rotating the bar at 1760 rpm.

However, following the successful demonstrations of excess heat that led to our paper at Nagoya\(^3\), experiments in Pyrex test tubes with a new batch of nickel foil failed to produce excess heat for 4 months. The heating values simply extended the calibration curve as seen in Figure 2. To generate this curve, power input was stepped by changing the current every 12 hours. There is a slight hysteresis to the curve as the current increased and then decreased.

After each current change there was a 12 hour wait for equilibrium. In this period the cell temperature and voltage were averaged over 2 hours on a datalogger with readings logged every 30 seconds. The change in cell voltage vs time is plotted in Figure 3 for 6 of the 13 steps with increasing current. Voltage rose at lower currents as labelled on the right. When the cell reached equilibrium temperature the next step was initiated. The rise in voltage was attributed to the resistance of the agglomerate. At higher currents, gassing apparently dispersed the agglomerate and cell voltage declined during the 12 hour period. This may partly explain why pulse power can enhance excess heating.

Four months of experimenting without producing excess heat led to considerable frustration and pointed to one difference in experimental conditions: early work used an old discoloured, hard and brittle nickel foil; later work used soft, malleable, shiny nickel of the same thickness. Since the stock of brittle nickel was exhausted and none was available from suppliers it had to be prepared. Parthasaradhy\(^4\) describes a method for electroplating nickel with a "hardness" of 400 VPN which demands plastic containers and muslin anode bags. This prompted an electroplating cell design which was then modified to include heater wells for the calibration of electrolysis experiments as described next.
Experiments in Plastic

The Plexiglass tube with base as seen in Figure 4 uses two nickel anodes to provide a uniform current density at the cathode. Anode bags were easily slipped on and off; these were made of close woven cotton/polyester. The heater wells were made of Teflon tubes. Cell temperature was observed with an Omega self-adhesive thermocouple on the exterior of the cell wall.

Figure 5 shows plots of cell voltage and heating vs time for this Plexiglass cell with an electroplated "hard" nickel cathode (36.4 cm²), Ni anodes (total 55 cm²) and 0.57M K₂CO₃. At the outset, the cell voltage was high. Anode bags introduced at the 8 hour mark were used to extract colloidal impurities which formed a gas bubble filled gel on the bag. When the bags were removed at the 25 hour mark the voltage dropped (presumably due to the loss of the resistive gel layer on the bags) and heating per watt increased slowly. Then the current was decreased to 45mA at 72 hours which further reduced cell voltage and increased heating to 10.5 °C/W. Calibration heating in this cell produced 6.5 °C/W. At 45mA the voltage rose slowly for 150 hours but was quite low (2 volts) and stable as described previously by Mills and Kneizys⁵ and Noninski⁶.

The higher heat per watt in this cell was found to be characteristic of several "hard" nickel cathodes and was quite different from the soft nickel of Figure 2. By exchanging cathodes, it was found that excess heat could be switched on and off in this experiment. Classical heating was observed with soft nickel, while "hard" nickel produced up to 12 °C/W (i.e. about 100% excess heat). An old electrode of brittle nickel used for earlier work³ was rejuvenated in 0.57M K₂CO₃/3% H₂O₂ according to a recipe of Mills⁷ and it then achieved previous performance levels again close to 12 °C/W.

Figure 6 shows calibration and electrochemical heating levels for the Plexiglass cell using a soft nickel cathode which had been oxidized in air at 500 °C for an hour to blacken it like our original aged nickel. Calibration values with and without bags forms a continuous curve. Cell heating with anode bags in place in this instance was at the calibration level. When the bags were removed, cell heating produced considerable excess heat. However, these results must be considered preliminary until the roles of agglomerates and of metals are more fully appreciated.

These divergent results on Ni/K₂CO₃ reflect similar experiences on Pd/LiOD. Palladium rod produced excess heat⁸ from about 400 hours to 800 hours into a run which may reflect the time for it to be hardened by deuterium intrusion and perhaps before it cracked with embrittlement. Annealed palladium foils and rods subjected to ramped power often failed to produce excess power until the power ramps were repeated⁹, again suggesting a required time to harden. Alternatively, a palladium ball deformed by hammer blows into a fat dime shape¹⁰ produced excess heat within 15 hours. Another palladium foil that was cold worked¹¹ yielded excess heat after 30 current ramps (10 hours) although a replication experiment using palladium from the same batch was less successful; oddly, no mention was made of cold working the replication foil. The parallel successes for hardened or cold worked cathodes in light and heavy waters may be more than coincidence.
Conclusions
It is concluded that colloidal impurities affect excess heat cells that use ordinary water by raising the cell voltage and increasing resistive heating. Removal of these colloids can decrease cell voltage and improve the fraction of input power that is exhibited as excess cell heating. It is also concluded that "hardened" nickel samples prepared in three different ways all produced excess heat while soft nickel did not. This situation appears to parallel the experiences of heat production from palladium in heavy water.

Acknowledgements
The financial contribution of Energy, Mines and Resources Canada is greatly appreciated.

References


Figure 1. An electrochemical garden monster grown on Ni wire anode.

Figure 2. Heat vs input power for soft Ni cathode coincides with calibration heat.
Figure 3. Cell voltage vs time after a current increase.

Figure 4. Plexiglass cell with Ni cathode and bagged anodes.

Figure 5. Plexiglass cell volts and heating vs time, under various conditions.

Figure 6. Plexiglass cell calibration & heat vs input, with and without anode bags.