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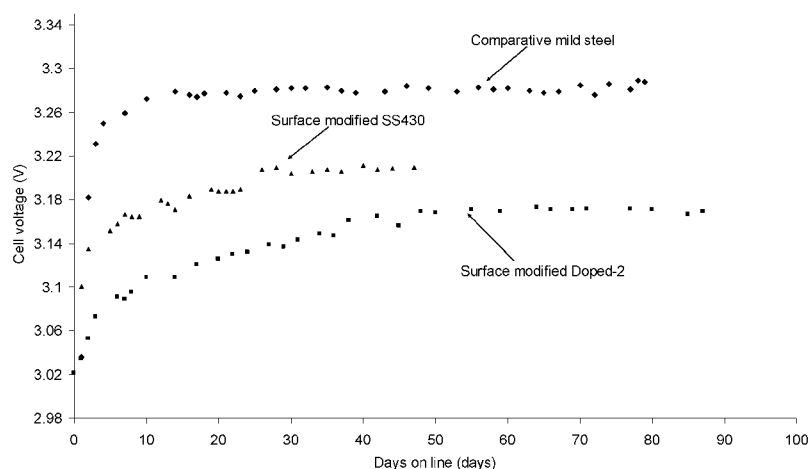
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(54) **Title:** SURFACE MODIFIED STAINLESS STEEL CATHODE FOR ELECTROLYSER

**FIG. 5**

(57) **Abstract:** Sodium chlorate is produced industrially via electrolysis of brine and is thus an energy intensive process. An improved cathode for this and other industrial processes is a low nickel content stainless steel whose surface has been suitably modified. With an appropriate amount of surface roughening, the cathode provides for improved overvoltages during electrolysis while still maintaining corrosion resistance.

SURFACE MODIFIED STAINLESS STEEL CATHODE FOR ELECTROLYSER

Technical Field

The present invention pertains to cathode electrodes for use in industrial electrolysis, such as electrolysis of brine to produce chlorate product. In particular, it pertains to surface modified, low
5 nickel content, stainless steel cathodes for such use.

Background

Sodium chlorate is produced industrially mainly by the electrolysis of sodium chloride brine to produce chlorine, sodium hydroxide and hydrogen. The chlorine and sodium hydroxide are
10 immediately reacted to form sodium hypochlorite, which is then converted to chlorate. In the overall electrolysis process, complex electrochemical and chemical reactions are involved that are dependent upon such parameters as temperature, pH, composition and concentration of electrolyte, anode and cathode potentials and over-voltages, and the design of the equipment and electrolytic system. The choices of cell parameters such as electrode sizes, thickness, materials, anode coating options and off-
15 gas are important to obtain optimal results.

The choice of material and configuration for the cathode electrode in the chlorate electrolyser is particularly important with regards to the efficiency of the electrolysis and to the durability of the cathode in the harsh conditions in the electrolyser. Material and design combinations are selected so
20 as to obtain the best combination possible of overvoltage characteristics during operation, along with corrosion and blister resistance, cost, manufacturability, and durability characteristics. If cathodes comprising coated substrates are employed, substrate compatibility with the coatings must be taken into account. Preferably any improved cathode electrode is able to replace those in current electrolyser designs, without requiring other major design and material changes to other components like the
25 carrier plates to which they are attached by welding.

Conventional chlorate electrolyser efficiency might be improved via improvements to the overpotential found at the cathode during the electrolysis process. According to a typical breakdown of losses incurred within the electrolyser, the cathode overpotential accounts for approximately 38%
30 (430 mV) of the total loss, with the other key losses relating to electrolyte resistance, anode overpotential, metallic resistance and “dichromate effect” (which results from film formation on the cathode when sodium dichromate is employed as a buffer and for suppressing the reduction of hypochlorite and chlorate ions at the cathode.)

In commercial mono-polar and hybrid chlorate electrolyser designs, the cathodes are typically uncoated carbon steel types like Domex grade steel, C1008 and Stahrmet®. The latter Stahrmet® cathodes use a select steel with specific elemental composition in order to prevent and/or reduce hydrogen blistering and embrittlement when in service. Such cathodes perform reasonably well in combination with conventional DSA® (Dimensionally Stable Anode) anodes in terms of cell voltage and overpotential over the normal range of operating conditions (e.g. current densities from 2.5 to 4.0 kA/m² and temperatures from 60 to 90 °C. They are also a relatively low cost component of the electrolyser.

Uncoated carbon steel electrodes however are susceptible to corrosion (rusting) which results in cathode thinning, undesirable metal ions entering the electrolyte, and decreased cathode life, even under normal operating conditions with cathodic protection. Over the expected life of the electrolyzers, there are typically shutdowns and power interruptions which accelerate the corrosion of the cathodes. Metal ions in the electrolyte deposit on the electrodes and can affect both the anode and cathode performance simultaneously via this type of fouling, yielding symptoms of both elevated cell potential and oxygen production, and resulting in higher operating cost. The cathodes will show predominantly pitting-type surface erosion distributed more or less uniformly throughout the working area. This type of corrosion is typical for carbon steel cathodes exposed to hypochlorite. Since the scale has to be removed during servicing and before re-use, the cathodes need to be mechanically cleaned (e.g. by sand-blasting) and acid-washed. A significant amount of material (mostly iron) is typically removed in this treatment such that carbon steel cathodes require a substantial corrosion allowance to compensate for the loss of material, thereby resulting in a requirement for thicker cathodes and thus reduced active electrode area per unit volume. Further, when cathodes are refurbished and put back into service, the gaps between cathodes and anodes in the electrolyser will increase causing an increase in voltage.

As an alternative, other materials may be considered for use as chlorate electrolyser cathodes. However, unlike in the related industrial chlor-alkali electrolysis process (in which sodium chloride brine undergoes electrolysis to form sodium hydroxide, hydrogen and chlorine products), cathodes based on nickel or which comprise a significant amount of nickel cannot be employed. The presence of nickel results in an increase in the rate of hypochlorite decomposition and thereby reduces product yield and produces higher levels of oxygen than normal. This presents a safety concern since the oxygen can potentially combine with the hydrogen that is present to achieve unsafe, explosive mixtures. Thus, cathodes which are nickel free or at least have low nickel content (e.g. less than about 6% by weight) are used for chlorate electrolysis.

Certain grades of stainless steel (e.g. ferritic, martensic, duplex, and precipitation-hardened) are low nickel content grades of stainless steel and can offer advantages over carbon steel with regards to their corrosion resistance characteristics. However, these types of stainless steels, and in fact stainless steels in general, at least as they are typically prepared for commercial use exhibit substantially higher overvoltages than carbon steel when used as a cathode in chlorate electrolysis.

As a further alternative, various coatings have been suggested in the art for purposes of preparing coated substrates for use as electrodes in brine electrolyzers. For instance, Canadian patent application CA2588906 discloses nanocrystalline alloys for use as coatings for chlorate electrolysis. RuO₂ type coatings have also been suggested as electrode coatings in brine electrolysis. However, cathodes using carbon steel substrates cannot be easily coated with typical precious metal and mixed oxide coatings containing Ru, Ir, Ti, or the like. When applied using conventional methods, there are adhesion and degradation issues. In turn, this results in durability issues for the coatings as they simply exfoliate or “flake off” when the underlying carbon steel substrate is corroded. (In US7122219, attempts were made to address this problem for electrodes intended for chlor-alkali electrolysis.) It has been very difficult to obtain a carbon steel coated cathode that matches the expected 5 to 8 year lifetime of standard commercial anodes in chlorate electrolyzers.

It is generally known that appropriate surface treatments of metal substrates (e.g. sandblasting) can result in improved adhesion of applied coatings. And it is known (e.g. as disclosed in US6017430) that grit-blasting the cathodes used in the electrolysis of aqueous alkali metal chloride solutions can reduce the hydrogen overvoltage at the cathode by increasing its surface area. However, it is also well known that surface smoothness is important for better corrosion resistance of stainless steels. Since stainless steels resist corrosion best when they are clean and smooth, low surface roughness has been particularly sought for use in extremely corrosive environments, e.g. the environment within a brine electrolyser.

Roughness is characterized in various ways in the industry. Roughness parameters such as arithmetic mean of roughness, denoted as R_a , and mean square of roughness, denoted as R_q , are commonly used to quantify surface roughness and are determined by standardized methods. In addition, surfaces may also be characterized by more qualitative terminology, such as “finish”. A No. 4 finish stainless steel is a general purpose polished finish, is duller than the other common finishes, and is commonly used for work surfaces or the like where appearance and cleanliness is important (e.g. for equipment used in the food, dairy, beverage, and pharmaceutical industries). As per ASTM A480, the R_a of a No. 4 finish may generally be up to 0.64 micrometers. R_a may be approximately 80% of R_q and so the R_q of a No. 4 finish would be somewhat less than 1 micrometer.

However, while there is a correlation between these various roughness characteristics and other characteristics such as appearance and corrosion resistance, two surfaces can have the same R_a (and/or the same R_q) and yet have a different appearance or resistance to corrosion depending on how the surface condition was obtained. For instance, such characteristics can vary depending on whether the finish is directional or random (e.g. was obtained by belt abrasion or by sandblasting respectively) and on other factors such as orientation.

While the industrial chlorate electrolysis process is quite advanced, there still remains a desire for ever greater efficiency, electrolyser lifetime, and reduction in cost.

Summary

The present invention addresses these needs by providing improved electrolysis cathodes which exhibit both desirable overvoltage and corrosion resistance characteristics. For instance, overvoltages similar or better to those seen with carbon steel cathodes can be obtained along with corrosion resistance similar to that expected from cathodes made with conventional stainless steels. Such cathodes are useful for chlorate electrolysis and may be for other industrial electrolysis processes.

Surprisingly, cathodes made with certain nickel free or low nickel content (e.g. less than about 6% by weight) stainless steels can achieve both these characteristics if the surface has been modified or treated so as to obtain a certain surface roughness. Low nickel content stainless steels potentially suitable for this purpose include certain ferritic, martensitic, duplex, and precipitation-hardened stainless steels. It can be advantageous to employ a stainless steel comprising one or more stabilizing dopants. Suitable dopants include Cu, Mo, N, Nb, Sn, Ti, V, and W. It can also be advantageous to employ a stainless steel with low carbon content, e.g. less than about 0.03% by weight and preferably less than about 0.005% by weight in certain embodiments.

In particular, the low nickel content stainless steel can be a ferritic stainless steel such as a 430, 430D, 432, or 436S grade of stainless steel or a ferritic stainless steel comprising a Mo, Sn, Ti, and/or V dopant. Ferritic grades of stainless steel typically contain impurities of phosphorus and sulfur. It can be preferable for the stainless steel to comprise less than about 0.03% by weight phosphorus and less than about 0.003% by weight sulfur. Further, the low nickel content stainless steel can be a duplex stainless steel such as a S31803, S32101, S32205, S32304, S32404, S82011, or S82122 lean/low alloy grade of duplex stainless steel.

A surface roughness R_q in the range from between about 1.0 and 5.0 micrometers has been found to be suitable with regards to overvoltage and may also provide improved corrosion resistance. In particular, a ferritic stainless steel with a R_q less than about 2.5 micrometers appears suitable.

- 5 The surface modified stainless steel can be used directly (uncoated) as a cathode in an industrial electrolyser, such as a sodium chlorate, potassium chlorate or sodium perchlorate electrolyser. For use in such an embodiment, the cathode can be welded to a carrier plate made of carbon steel or stainless steel. Advantageously, if the cathode is welded to a carrier plate made of an appropriate stainless steel and the remainder of the electrolyser is also made of an appropriate stainless, the electrolyser does not
10 need to employ a cathodic protection unit.

Alternatively the surface modified stainless steel can be used as a substrate in a cathode which comprises an electrolysis enhancing coating applied to it. The surface modification can improve the adhesion of a suitable electrolysis enhancing coating. And further, although the overvoltage
15 advantage of the surface modified substrate may not be immediately necessary or observed in a new coated cathode, when the coating eventually wears away, the underlying surface modified stainless steel substrate is exposed. At this time, the exposed substrate now exhibits the combined overvoltage and corrosion resistance advantages of the invention and thereby extends the useful life of the cathode over that of the current industry standard Stahrmel®.

20 Thus, the overvoltage of a chlorate electrolyser cathode can be reduced during electrolysis of brine, while maintaining resistance of the cathode to corrosion, by roughening the surface of a low nickel content stainless steel cathode to a surface roughness R_q between about 1.0 and 5.0 micrometers. A variety of roughening methods may be employed, for instance sandblasting the cathode surface with
25 aluminum oxide powder.

Brief Description of the Drawings

Figure 1 compares the mini-cell voltage versus current density plots for several representative surface modified SS430 cathode samples, a comparative SS430 sample and a conventional Mild steel sample.

Figure 2 plots the mini-cell voltages observed at several representative current densities as a function
30 of the surface roughness for the SS430 cathode samples in the Examples.

Figure 3 compares the mini-cell voltage versus current density plots for various RuO_2 coated, surface modified SS430 cathode samples to a conventional Mild steel sample.

Figure 4 compares the mini-cell voltage versus current density plots for several representative surface modified ferritic cathode samples to a conventional Mild steel sample.

Figure 5 compares the plot of electrolysis pilot cell voltage versus days of operation at normal conditions for a cell comprising a conventional carbon steel cathode to those of cells comprising a SS430 cathode and a doped ferritic cathode which have been surface treated in accordance with the invention.

Detailed Description

Unless the context requires otherwise, throughout this specification and claims, the words "comprise", "comprising" and the like are to be construed in an open, inclusive sense. The words "a", "an", and the like are to be considered as meaning at least one and not limited to just one.

In addition, the following definitions are intended. In a numerical context, the word "about" is to be construed as meaning plus or minus 10%.

Stainless steel refers to a steel alloy with a minimum of 10.5% chromium content by mass.

Surface roughness R_q refers to the mean square of roughness as determined according to standards JIS2001 or ISO1997 and are what were used in the Examples below.

And herein, an electrolysis enhancing coating refers to a coating on an electrode in a chlorate electrolyser which results in a reduction in overvoltage during normal operation. Various such coating compositions are known in the art and typically comprise noble metal compositions such as RuO_2 .

In otherwise conventional electrolyzers for the industrial production of chlorate, certain low nickel content stainless steels have unexpectedly been found to be improved materials for use as cathode electrodes if their surfaces have been appropriately modified. Such cathodes show desirable overvoltage characteristics that are similar to or better than those obtained with carbon steel, while maintaining the desirable corrosion resistance expected from conventional stainless steel.

Suitable stainless steels are nickel free or have nickel content less than about 6% by weight. Several classes of stainless steels meet this requirement including ferritic, martensitic, duplex, and precipitation-hardened stainless steels. In addition, it can be of advantage to employ one or more stabilizing dopants in the stainless steel. Suitable such dopants include Cu, Mo, N, Nb, Sn, Ti, V, and W. It may also be of advantage to employ a stainless steel with low carbon content or very low carbon content, namely less than about 0.03 or less than about 0.005% by weight carbon content. (Carbon is known to promote hydrogen embrittlement by reaction with hydrogen to form methane. Thus, the

more carbon present in a hydrogen evolution cathode, the more likely it may be for methane to form in the cathode substrate. Accumulation of methane in grain boundaries or defects (such as inclusions of the sulfide or oxide type) in the substrate can cause blistering and embrittlement of the substrate.)

In particular, ferritic stainless steels can be suitable and are distinguished by the primary alloying element being chromium (ranging from about 10.5 to 27 wt%), which provides a stable ferritic structure at all temperatures. Due to their low carbon content, ferritic stainless steels have limited strength but can have good ductility and they work harden very little. The toughness of these alloys is quite low, but this is not an essential requirement for use as a cathode in an electrolyser. Unprotected, a Cr-rich ferritic stainless steel eventually corrodes in hot chlorinated liquor but not as quickly as carbon steel does. The Cr-rich stainless steel hydrogen release over-potential is higher than that for carbon steel. The Cr-rich stainless steel in contact with carbon steel does not appear to corrode quicker since the former does not act as a sacrificial anode for the latter. This is important for implementation as a replacement or upgrade for a carbon steel cathode in commercial electrolyzers since the cathode side of the carrier plate in the electrolyser may still be carbon steel and thus a ferritic stainless steel will be compatible therewith. Cromgard® is an example of a potentially suitable ferritic stainless steel having about 12% Cr content and exhibiting good weldability. Alternatively of course, carrier plates may be employed that are also made of a suitable grade of stainless steel, thereby eliminating all carbon steel present and thus any issue with use of dissimilar metals.

Testing has shown that ferritic grades including 430, 430D, 432, and 436S can be suitable. And in particular, certain extra low interstitial ferritic type stainless steels comprising dopants have shown marked improvement in electrolyser overvoltage. It is also expected that other ferritic grades would be suitable, including 444 grade which comprises Mo, Nb, and V dopants (in exemplary amounts of about 1.8, 1.6, and 0.06% by weight respectively) and 434, 439, 441, 442 and 446 grades of stainless steel.

Other low nickel content ferritic or martensitic stainless steel alloys may contain molybdenum, providing them with corrosion resistance far superior to conventional carbon steel in most chemical environments. There are many types of these alloys which contain other elements like Mn, Si, Al, Se, Cb, Cu, Ta, N, and W which may offer additional benefits with regards electrical conductivity, surface activity, manufacturability and/or durability for such applications. For instance, duplex stainless steel, also known as ferritic-austenitic stainless steel, in which the Cr range is from about 4 – 18 wt% has better welding characteristics than ferritic stainless steel. Certain duplex stainless steel alloys, such as UNS numbers S32101, S32304, and S82441 grades (e.g. commercial LDX 2101™, LDX 2304™ or LDX 2404™ respectively) along with S31803, S32205, and S82122, can be expected to offer advantages including superior corrosion resistance, manufacturability (also having better welding

characteristics than ferritic stainless steel), and commercial availability in addition to performance advantages.

In order to obtain overvoltages similar to or better than that obtained with carbon steel, the surface of a conventional low nickel content stainless steel has to be roughened, typically such that its surface roughness R_q is greater than about 1.0 micrometers. For instance, the surface roughness R_q of a conventional 430 grade of ferritic stainless steel intended for use in the Examples below was less than 0.1 micrometers as-obtained. Its surface was suitably roughened using a sandblasting method and aluminum oxide powder.

Any of various methods known in the art may be contemplated for roughening the stainless steel surface. For instance, along with sandblasting, alternative abrasion techniques (e.g. table blasting, belt blasting, cylinder blasting) and methods including chemical etching, micro-machining, and micro-milling can also be used to suitably increase surface roughness. However, as is also known in the art, the surface characteristics may vary according to the detailed method used. For instance, the surface characteristics obtained via sandblasting can vary according to the type of powder used (e.g. aluminum oxide, sodium bicarbonate, silicon carbide, glass bead, crushed glass), powder particle size, nozzle size, pressure, distance, angle, and so on. And processes like photochemical machining allow for the milling and grinding of the surface to more precise depths and to larger R_q values.

While increased surface roughness of the low nickel content stainless steel is required in order to obtain a desirable overvoltage, excessive roughness may result in unacceptable corrosion characteristics. Based on the Examples below, surface roughness R_q values up to 5.0 micrometers may still be acceptable. In certain cases, values up to about 2.5 micrometers may be preferred. It may however be necessary to maintain the cathodic protection provided to the cathode as a result of normal operation of an electrolyser or provide alternative means of protection during instances of power outages or shutdown.

Surface modified low nickel content stainless steel cathodes can replace present conventional carbon steel cathodes while advantageously providing better durability, cost and performance. Such cathodes can be welded successfully to standard carbon steel carrier plates for use in industrial electrolysers as a substitute for conventional carbon steel cathodes. Welding can be accomplished via different combinations of filler wire (e.g. welding rod), shielding gases, backup purge, and welding parameters (including current, voltage, and rate). Thus, major electrolyser design changes need not be implemented for either refurbished electrolyser cells and for new electrolyser systems. Further, it may be possible to incorporate cathodes of the invention in future designs (e.g. of the bipolar type).

Alternatively, if the industrial electrolyser is made entirely of an appropriate stainless steel and thus for instance the cathodes are welded to carrier plates made of stainless steel, the electrolyser may do without cathodic protection and thus may not need to employ a cathodic protection unit.

5 Other advantages of the invention include the energy savings obtained from the lower cathodic overpotential. And with better corrosion resistance of some grades, thinner cathode embodiments may be considered yielding more product per unit volume of electrolyser and/or allowing for reduced size and cost for the same level of output. It is also likely that such surface modified cathodes will be more compatible with electrolysis enhancing coatings in terms of adhesion and durability due to the
10 “anchoring effect” created by the rougher finish and avoidance of the failure mechanism associated with carbon steel corrosion. And even if no significant advantage was obtained, once a coating has worn away or otherwise failed, the underlying surface modified stainless steel substrate would be expected to continue providing for normal operation and survive substantially longer than a conventional carbon steel substrate, thereby extending the useful life of such coated cathodes.

15 The following Examples have been included to illustrate certain aspects of the invention but should not be construed as limiting in any way.

20 Examples

Mini-cell testing:

A series of cathode material samples was tested in a laboratory mini-cell under static conditions but otherwise similar to those experienced in a commercial chlorate electrolyser. The mini-cell
25 construction used a cathode material sample as the cell cathode and used a conditioned DSA® as the cell anode. Both of the electrodes were flat sheets. The active test surface area was about 2 cm² and the gap between them was 5.8 mm. The electrolyte was an aqueous solution of NaClO₃/NaCl/Na₂Cr₂O₇ in concentrations of 450/115/5 gpl. The electrodes were immersed in the electrolyte at a test temperature of 80°C. Unlike commercial electrolysers, the electrolyte was not
30 circulating during testing and no continuing brine feed was supplied.

Where indicated, the various cathode material samples were surface modified and their roughness measured prior to assembling into the mini-cell. Fresh electrolyte was then added, heated to the test temperature, and polarization testing was performed which involved ramping the current density
35 applied from 0.5 up to 6 kA/m² while recording the cell voltage. The test was then stopped and the sample electrode inspected for evidence of corrosion.

Surface roughness, R_q , was determined using a Mitutoyo Surftest SJ210. Six surface roughness samplings were performed at random locations on each cathode material sample over a sampling length of 2.5 to 6 inches and the maximum deviations from the mean line determined for each sampling. The R_q reported was the square root of the arithmetic mean of the squares of these six deviations.

The unmodified cathode material samples tested included:

- Stahmet® mild steel with a measured R_q of 2.16 μm (denoted “Mild steel” in the Figures and Tables)
- 420A grade stainless steel (SS420A) with a supplier’s 2D mill finish and having a measured R_q of 0.26 μm (denoted “SS420A-0.26 μm ” in the Figures and Tables)
- 430 grade stainless steel (SS430) with a supplier’s bright mill finish and having a measured R_q of 0.06 μm (denoted “SS430-0.06 μm ” in the Figures and Tables)

(Note: both stainless steel samples had similar low nickel content, i.e. < 0.25 wt%, and both comprised amounts of Mn, S, P, Si, Cu and Mo. The SS420A grade had C and Cr contents of 0.25% and 12.83% by weight and also had a trace amount of Al. The SS430 grade had C, Cr, and N contents of 0.04%, 16.64%, and 0.03% by weight.)

Surface modified cathode material samples were prepared by taking similar SS420A and SS430 samples as above and subjecting them to a manual sandblasting process using a 120 grit aluminum oxide powder. The surface modified samples tested included:

- SS420A sandblasted to a measured surface roughness R_q of 1.73 μm (denoted “SS420-1.73 μm ” in the Figures and Tables)
- a series of SS430 samples sandblasted to various surface roughnesses R_q ranging from 0.86 to 4.62 μm (denoted “SS430-0.86 μm ” to “SS430-4.62 μm ” in accordance with their surface roughness in the Figures and Tables)

Further, RuO_2 coated, surface modified SS430 cathode material samples were prepared with a range of RuO_2 loadings. Cathode material samples were made by initially sandblasting 430 stainless steel samples as above to and then coating in-house using RuCl_3 solution followed by a heat treatment procedure. Specifically, samples were degreased, rinsed, and then etched with a 10% HCl solution for 5 minutes at room temperature. After rinsing again and drying, a solution of RuCl_3 in an organic solvent was applied. The coated samples were dried and then heat treated at about 420 °C for 20 minutes. More than one application of coating and heat treatment was used to obtain the greater loading amounts.

The RuO₂ coated, surface modified samples prepared and tested are summarized in Table 1 below:

Table 1. RuO₂ coated, surface modified samples

Sample name	R _q (μm)	RuO ₂ loading (g/m ²)
RuO ₂ #1	1.6	2.77
RuO ₂ #2	1.55	4.33
RuO ₂ #3	1.45	5.54
RuO ₂ #4	1.45	6.1

- 5 Mini-cells comprising each of these cathode material samples were then assembled and subjected to polarization testing over a range of current densities from 0.5 to 6 kA/m² at 80°C.

Table 2 summarizes the data obtained for the conventional Mild steel sample, the SS420A-0.26 μm sample, and the surface modified cathode sample SS420-1.73 μm. Table 2 shows the laboratory mini-cell voltage for each cathode sample at the various current densities tested. As is evident from the data, the cell with the unmodified SS420A-0.26 μm cathode operated at a substantially greater cell voltage or overvoltage than the cell with the conventional Mild steel cathode. However, the cell with the surface modified SS420-1.73 μm cathode operated at even somewhat lower cell voltages than the cell with the conventional Mild steel cathode. Specifically at 4 kA/m², the unmodified SS420A-0.26 μm cathode cell voltage was 150 mV higher than the Mild steel cell voltage, while the surface modified SS420-1.73 μm cathode cell voltage was 25 mV less than the Mild steel cell voltage.

Table 2. Cell voltage versus current density for SS420 samples tested

Current density (kA/m ²)	Cell voltage (volts)		
	Mild steel	SS420-0.26 μm	SS420-1.73 μm
0.5	2.53	2.60	2.46
1.0	2.67	2.76	2.62
1.5	2.78	2.88	2.74
2.0	2.87	3.00	2.84
2.5	2.97	3.10	2.93
3.0	3.06	3.20	3.03
3.5	3.16	3.31	3.12
4.0	3.25	3.40	3.22
4.5	3.34	3.49	3.31
5.0	3.41	3.57	3.41
5.5	3.50	3.67	3.50
6.0	3.60	3.76	3.59

Following testing, the cathode samples were inspected. Both SS420 samples were found to have corroded substantially however.

5 Table 3 summarizes the data obtained with the series of SS430 samples sandblasted to various surface roughnesses and compares them to the comparative unmodified SS430 and mild steel cathode samples. The laboratory mini-cell voltage for each cathode sample at the various current densities tested are shown.

Table 3. Cell voltage versus current density for SS430 samples tested

Current density (kA/m ²)	Cell voltage (volts)													
	Mild steel	SS430 0.06 μm	SS430 0.86 μm	SS430 1.05 μm	SS430 1.15 μm	SS430 1.70 μm	SS430 1.76 μm	SS430 1.81 μm	SS430 2.14 μm	SS430 2.25 μm	SS430 2.49 μm	SS430 2.82 μm	SS430 3.48 μm	SS430 4.62 μm
0.5	2.53	2.73	2.61	2.57	2.53	2.45	2.47	2.45	2.46	2.51	2.49	2.52	2.56	2.50
1.0	2.67	2.91	2.78	2.72	2.68	2.60	2.60	2.60	2.62	2.65	2.63	2.66	2.71	2.65
1.5	2.78	3.02	2.92	2.85	2.80	2.71	2.71	2.71	2.73	2.77	2.74	2.78	2.83	2.76
2.0	2.87	3.13	3.02	2.96	2.90	2.82	2.82	2.81	2.84	2.86	2.84	2.88	2.94	2.87
2.5	2.97	3.22	3.13	3.06	3.01	2.91	2.91	2.91	2.94	2.96	2.94	2.98	3.04	2.96
3.0	3.06	3.31	3.24	3.17	3.09	3.00	3.01	3.00	3.03	3.06	3.05	3.08	3.13	3.05
3.5	3.16	3.39	3.33	3.26	3.19	3.08	3.10	3.09	3.13	3.15	3.13	3.17	3.23	3.15
4.0	3.25	3.48	3.42	3.35	3.28	3.19	3.18	3.18	3.22	3.24	3.23	3.27	3.32	3.24
4.5	3.34	3.55	3.51	3.44	3.37	3.27	3.28	3.27	3.32	3.33	3.33	3.35	3.41	3.34
5.0	3.41	3.66	3.59	3.53	3.46	3.36	3.36	3.36	3.39	3.42	3.41	3.45	3.51	3.43
5.5	3.50	3.71	3.70	3.62	3.54	3.45	3.46	3.46	3.47	3.50	3.49	3.55	3.60	3.53
6.0	3.60	3.80	3.77	3.70	3.62	3.54	3.55	3.55	3.56	3.59	3.58	3.63	3.68	3.61

Figure 1 compares the mini-cell voltage versus current density plots for several representative surface modified SS430 cathode samples, the comparative unmodified SS430-0.06 μm sample and the conventional Mild steel sample. (A line through the data for the Mild steel sample is provided as a guide to the eye.) As can be seen in Figure 1, the cell with the unmodified SS430-0.06 μm cathode also operated at a substantially greater overvoltage than the cell with the conventional Mild steel cathode. As for the surface modified SS430 samples, the overvoltage generally improved with increasing surface roughness up to a R_q of about 1.70 μm . Mini-cells with SS430 cathodes having surface roughnesses less than or about 1.15 μm had lower operating voltages than the cell with the unmodified SS430-0.06 μm cathode but were not as low as the cell with the conventional Mild steel cathode. However, mini-cells with SS430 cathodes having surface roughnesses of about 1.70 μm or greater had similar or lower operating voltages than the cell with the conventional Mild steel cathode. The increase in surface roughness to 1.81 μm (not shown in Figure 1 but see Table 3) however did not seem to significantly reduce the operating cell voltage further. Specifically at 4 kA/m^2 , the unmodified SS430-0.06 μm cathode cell voltage was about 230 mV higher than the Mild steel cell voltage, while the SS430-1.81 μm cathode cell voltage was about 70 mV less than the Mild steel cell voltage.

Figure 2 plots the mini-cell voltages observed at several representative current densities as a function of surface roughness of the SS430 cathode samples. Specifically, the mini-cell voltages at 2, 3 and 4 kA/m^2 are plotted. As would be expected, the mini-cell voltage increases with current density used. And initially, the mini-cell voltage decreases with surface roughness. However, unexpectedly the mini-cell voltages at each current density seem to be at their lowest at surface roughnesses of about 1.8 μm .

Figure 3 compares the mini-cell voltage versus current density plots for the various RuO_2 coated, surface modified SS430 cathode samples to the conventional Mild steel sample. As is seen in Figure 3, every cell with a RuO_2 coated, surface modified SS430 cathode operated at a substantially lower cell voltage than the cell with the conventional Mild steel cathode. However, based on the testing performed, the amount of RuO_2 loading did not affect the cell voltage significantly. At 4 kA/m^2 , the RuO_2 coated, surface modified SS430 cathode cell voltages were substantially lower than the Mild steel cathode cell voltage, i.e. about 240-280 mV lower.

Following all the above SS430 and RuO_2 coated sample testing, there was no visible corrosion observed on any of the samples.

Another series of ferritic cathode material samples was obtained, surface modified, and tested in a laboratory mini-cell as described above and/or were corrosion tested as described later below. The samples here included the following:

- 5 - 430 grade stainless steel with a composition of 0.042% C, 0.36% Si, 0.48% Mn, 0.031% P, 0.0015% S, 16.13% Cr, 0.15% Ni, 0.041% N by weight, the remainder being Fe and having a measured R_q of 2.13 μm after sand blasting (denoted “SS430” in Figure 4)
- 10 - 430D grade stainless steel with a composition of 0.005% C, 0.1% Si, 0.11% Mn, 0.025% P, 0.002% S, 16.39% Cr, 0.29% Ti by weight, the remainder being Fe and having a measured R_q of 2.1 μm after sand blasting (denoted “SS430D” in Figure 4)
- 15 - 432 grade stainless steel with a composition of 0.004% C, 0.1% Si, 0.08% Mn, 0.022% P, 0.001% S, 17.20% Cr, 0% Ni, 0.18%Ti, 0.01% N, 0.48% Mo, 0.02% Cu, by weight, the remainder being Fe and having a measured R_q of 1.89 μm after sand blasting (denoted “432” but not shown in Figure 4)
- 20 - 436S grade stainless steel with a composition of 0.005% C, 0.1% Si, 0.09% Mn, 0.022% P, 0.002% S, 17.2% Cr, 0.23% Ti, 0.011% N by weight, the remainder being Fe and having a measured R_q of 2.09 μm after sand blasting (denoted “SS436S” in Figure 4)
- 25 - LDX2205 grade stainless steel with a composition of 0.018% C, 0.38% Si, 1.54% Mn, 0.023% P, 0.001% S, 22.50% Cr, 5.70% Ni, 0.017% N, 3.10% Mo by weight, the remainder being Fe and having a measured R_q of 1.73 μm after sand blasting (denoted “LDX2205” but not shown in Figure 4)
- 30 - a first doped grade of stainless steel with a composition of 0.004% C, 0.12% Si, 0.10% Mn, 0.024% P, 0.001% S, 14.4% Cr, 0.11% Sn, 0.20% Nb+Ti combined, 0.010% N by weight, the remainder being Fe and having a measured R_q of 2.35 μm after sand blasting (denoted “Doped-1” in Figure 4)
- 35 - a second doped grade of stainless steel with a composition of 0.005% C, 0.07% Si, 0.06% Mn, 0.020% P, 0.001% S, 16.4% Cr, 0.31% Sn, 0.22% Nb+Ti combined, 0.010% N by weight, the remainder being Fe and having a measured R_q of 2.14 μm after sand blasting (denoted “Doped-2” in Figure 4)

Figure 4 compares the mini-cell voltage versus current density plots obtained for these surface modified ferritic and surface modified doped ferritic cathode samples to that of the conventional Mild steel sample of Figure 1. (No test was performed on the 432 sample and thus it does not appear in Figure 4. And only the voltage at 4 kA/m² was obtained on the LDX2205 sample and thus it too does not appear in Figure 4. This voltage for the LDX2205 sample was 3.18 volts.) In all measured cases, the results for the surface modified samples were comparable to or better than the conventional Mild steel sample.

To obtain additional information relating to corrosion, the aforementioned samples including the conventional Mild steel sample were also subjected to a corrosion test in which individual samples were exposed to corrosive, circulating “hypo” electrolyte from a pilot scale chlorate reactor. (The “hypo” comprised an approximate 4 g/L solution of HClO and NaClO, which circulated at a flow rate of 60 L/h, at about 70° C, and was obtained from the reactor operating at a current density of 4 kA/m².) The samples were approximately 80 mm x 35 mm in area and about 3 mm thick and they were exposed to the electrolyte for a period of up to 5 hours. Corrosion rates were then determined based on the loss of weight from the samples resulting from this exposure (recorded as weight loss per unit area and time). Table 4 summarizes some of the corrosion rates observed.

Table 4. Corrosion rates observed

Sample	Mild steel	430	430D	432	436S	LDX2205	Doped-1	Doped-2
Corrosion rate (g/m ² -h)	31.2	30.6	37.2	32.9	27.7	0.01	39.7	24.4

The corrosion rates for all the samples tested was considered acceptable. (Note that the corrosion rate measured for the LDX2205 sample was very low. While correct, other testing suggested that attention should be paid to crevice corrosion as it may be much more significant.)

These examples suggest that SS430, SS430D, SS436, and doped ferritic stainless steel based cathodes might be appropriately surface modified so as to provide similar or better overvoltage performance to that of a conventional mild steel cathode in a chlorate electrolyser, while still maintaining an acceptable resistance to corrosion.

Pilot cell testing:

Comparison testing was performed in larger pilot scale electrochemical cells on a surface modified SS430 cathode (having a composition similar to that of the SS430 sample of Figure 4), a surface modified Doped-2 type cathode (having a composition similar to that of the Doped-2 sample of Figure 4) and on a conventional Stahrmel® mild steel cathode under the same conditions to those experienced in a commercial chlorate electrolyser. The pilot cells employed flat sheet cathodes that were 19 square inches in active area, the same commercially available anodes (DSA with a RuO₂ coating), and an electrolyte comprising an aqueous solution of sodium chlorate, sodium chloride, and sodium dichromate and having NaClO₃/NaCl/Na₂Cr₂O₇ concentrations of 450/110/5 gpl. Electrolyte flowed through the cell at a rate of 0.8 litre/amp-hour and was controlled to a pH of 6.0. During the testing the temperature ranged from 80°C to 90°C and the current density from 2 kA/m² to 4 kA/m². The pilot cell voltage was recorded during testing and also the oxygen concentration in the off-gases generated by the cell was monitored. Oxygen is an undesirable by-product in this type of electrolysis. A higher oxygen concentration in the off-gases is indicative of lower current efficiency (i.e. more energy being consumed to produce the same amount of sodium chlorate). Further, higher oxygen concentrations pose a safety concern when mixed with hydrogen gas also being produced. (Many factors can affect oxygen concentration including both electrode materials. While this is not a direct indicator of electrode corrosion it is a very important criterion to consider with regards to electrode selection.)

The cathodes tested again included a conventional comparative Stahrmel® mild steel cathode with a measured R_q of 2.16 µm, a SS430 cathode which had been sandblasted to a measured R_q of 1.54 µm, and a Doped-2 type stainless steel cathode which had been sandblasted to a measured R_q of 1.91 µm.

Initially, all cells were conditioned by operating at a reduced temperature and current density (80°C and 2 kA/m²) from those used during normal production electrolysis (90°C and 4 kA/m²). Over the course of 1-6 days, the temperature and current density were increased to the 90°C and 4 kA/m² values normally used for production electrolysis. Operation continued at these settings while the cell voltages stabilized. During conditioning, the cell voltages drift up over the first two to three weeks or so of operation. This is a normal effect and is due to conditioning of the DSA® anode and cathode polarization. Figure 5 compares the pilot cell operating voltages versus days of operation at normal conditions after the cell voltages had stabilized. (In Figure 5, the voltages from day 12 and onwards are shown. Note: the comparative mild steel cathode had been preconditioned for up to an additional 12 days.) . As is evident in Figure 5, the cell with the surface modified SS430 cathode has a markedly lower cell voltage than the comparative cell. After 12 days of conditioning, the surface modified SS430 cathode based cell was operating at 3.18 Volts and the oxygen concentration in the off-gases was a low 1.7%. Remarkably, the cell with the surface modified Doped-2 series cathode had an even lower cell voltage than that of the surface modified SS430 cathode and its superior performance was maintained for more than 85 days of operation.

To obtain an indication of the corrosion resistance of the surface modified SS430 cathode under these normal pilot cell operating conditions, approximately 1200ml of the electrolyte from the cell was filtered through 934-AH Glass Microfiber filter paper. No discoloration was seen in the filter paper suggesting no evidence of corrosion in the electrolyte after 20 days of pilot cell operation under normal operating conditions.

Again with regards to the surface modified SS430 cathode evaluation, testing continued at normal production electrolysis conditions for a total of 46 days during which time there was cathodic protection. Thereafter, the pilot cell was subjected to a power interruption test. This test evaluates corrosion resistance in the event of a shutdown of the electrolyser during which time there is no cathodic protection. The test comprised shutting off power three times for five minute periods with five minute periods of normal operation in between. Again, an electrolyte sample was taken and filtered through filter paper. This time, evidence of cathode corrosion was observed. However, unlike that observed on mild steel cathodes, the corrosion pattern on the SS430 cathode was localized (e.g. pitting) and not over the entire surface. Thus an improvement over mild steel is indicated and it would be expected that coatings over the majority of the SS430 surface would be unaffected.

An indication of the corrosion resistance of the surface modified Doped-2 cathode was obtained in a like manner by filtering electrolyte from its pilot cell and checking for residue and discoloration. Again, electrolyte samples were taken after normal pilot cell operating conditions and also after a power interruption test. In this case, the pilot cell was operated normally for 137 days while still maintaining a markedly low cell voltage under 3.21 volts. An electrolyte sample was then taken, and the cell was subjected to the power interruption test, after which another electrolyte sample was taken. Again, no discoloration was seen in the filter paper suggesting no evidence of corrosion in the electrolyte after 137 days of normal pilot cell operation. And again, evidence of corrosion was seen after the power interruption, but again the corrosion pattern on the Doped-2 cathode was localized, the discoloration of the filter paper was modest, and an improvement over mild steel is indicated.

This example demonstrates a significantly improved overvoltage for the cells comprising the surface modified SS430 and Doped-2 series cathodes as well as improved corrosion resistance.

All of the above U.S. patents, U.S. patent applications, foreign patents, foreign patent applications and non-patent publications referred to in this specification, are incorporated herein by reference in their entirety.

While particular elements, embodiments and applications of the present invention have been shown and described, it will be understood, of course, that the invention is not limited thereto since modifications may be made by those skilled in the art without departing from the spirit and scope of the present disclosure, particularly in light of the foregoing teachings. For instance, while the preceding description and examples were directed at chlorate electrolyzers, the invention might instead be useable for chlor-alkali production, hydrogen electrolysis, desalination of seawater or other industrial electrochemical applications used for chemical production requiring an active, low cost, chemically resistant cathode electrode material (e.g. conversion of carbon dioxide to liquid fuels and industrial chemicals). Such modifications are to be considered within the purview and scope of the claims appended hereto.

Claims

1. A cathode for an industrial electrolyser comprising a stainless steel electrode comprising less than about 6% by weight nickel and characterized by a surface roughness R_q between about 1.0 and 5.0 micrometers.
2. The cathode of claim 1 wherein the stainless steel electrode is characterized by a surface roughness R_q less than about 2.5 micrometers.
3. The cathode of claim 1 wherein the stainless steel is a ferritic stainless steel.
4. The cathode of claim 3 wherein the stainless steel is selected from the group consisting of 430, 430D, 432, and 436S grades of ferritic stainless steel.
5. The cathode of claim 1 wherein the stainless steel comprises a stabilizing dopant selected from the group consisting of Cu, Mo, N, Nb, Sn, Ti, V, and W.
6. The cathode of claim 3 wherein the ferritic stainless steel comprises Mo dopant.
7. The cathode of claim 3 wherein the ferritic stainless steel comprises Sn dopant.
8. The cathode of claim 3 wherein the ferritic stainless steel comprises Ti dopant.
9. The cathode of claim 3 wherein the ferritic stainless steel comprises V dopant.
10. The cathode of claim 1 wherein the stainless steel is a duplex stainless steel.
11. The cathode of claim 10 wherein the stainless steel is selected from the group consisting of S31803, S32101, S32205, S32304, S82441, S82011, and S82122 grades of duplex stainless steel.
12. The cathode of claim 1 wherein the stainless steel comprises less than about 0.03% by weight carbon.
13. The cathode of claim 12 wherein the stainless steel comprises less than about 0.005% by weight carbon.

14. The cathode of claim 1 wherein the stainless steel comprises less than about 0.03% by weight phosphorus and less than about 0.003% by weight sulfur.

15. The cathode of claim 1 comprising an electrolysis enhancing coating applied to the low nickel
5 content stainless steel electrode.

16. An industrial electrolyser comprising the cathode of claim 1.

17. The industrial electrolyser of claim 16 wherein the industrial electrolyser is a sodium chlorate
10 electrolyser.

18. The industrial electrolyser of claim 16 wherein the cathode is welded to a carrier plate made of carbon steel or stainless steel.

15 19. The industrial electrolyser of claim 18 wherein the cathode is welded to a carrier plate made of stainless steel and the electrolyser is absent a cathodic protection unit.

20. A method of reducing the overvoltage of an industrial electrolyser cathode during electrolysis of brine while maintaining resistance of the cathode to corrosion, the method comprising roughening
20 the surface of a stainless steel cathode comprising less than about 6% by weight nickel to a surface roughness R_q between about 1.0 and 5.0 micrometers.

21. The method of claim 20 wherein the roughening comprises sandblasting the cathode surface with aluminum oxide powder.

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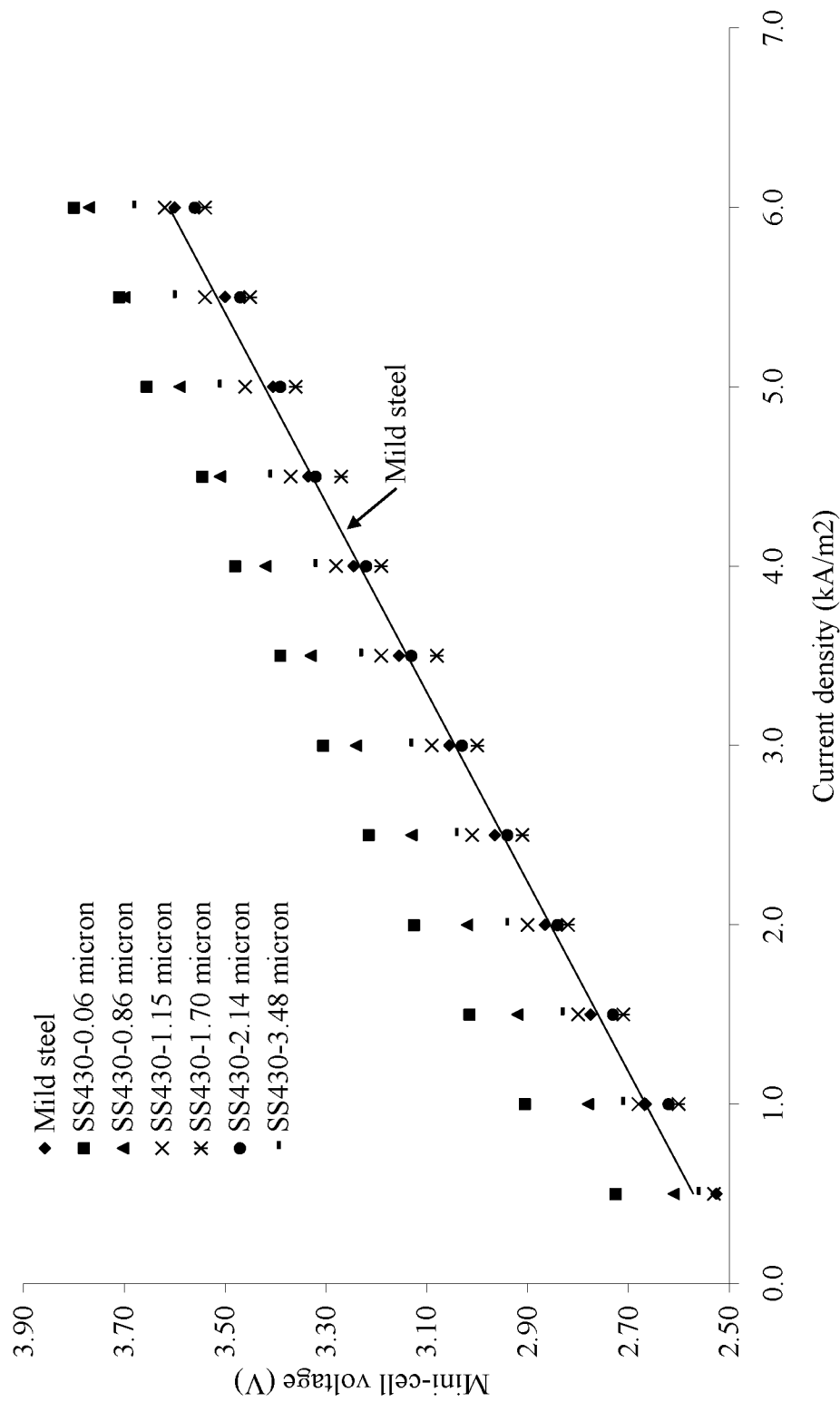


FIG. 1

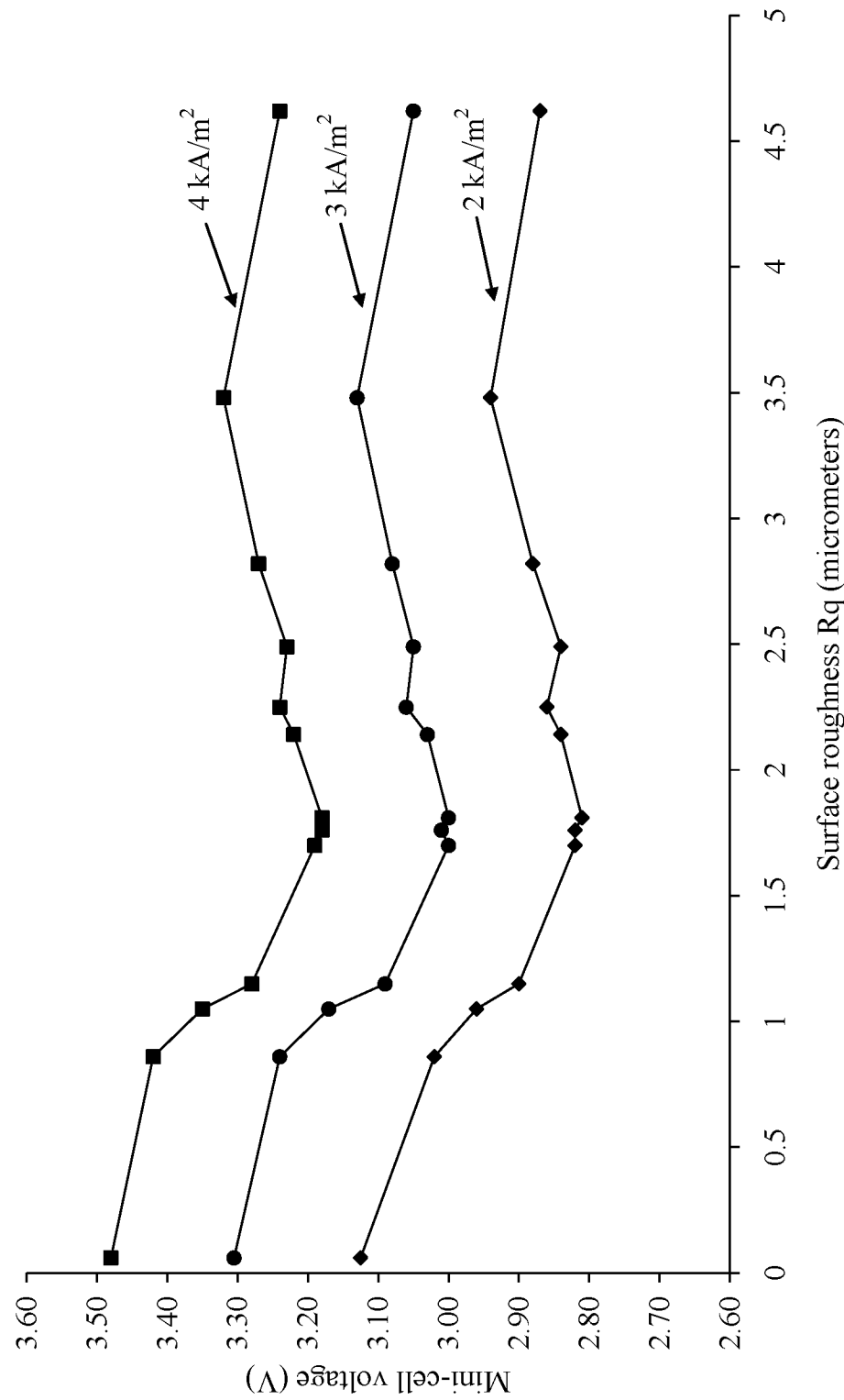


FIG. 2

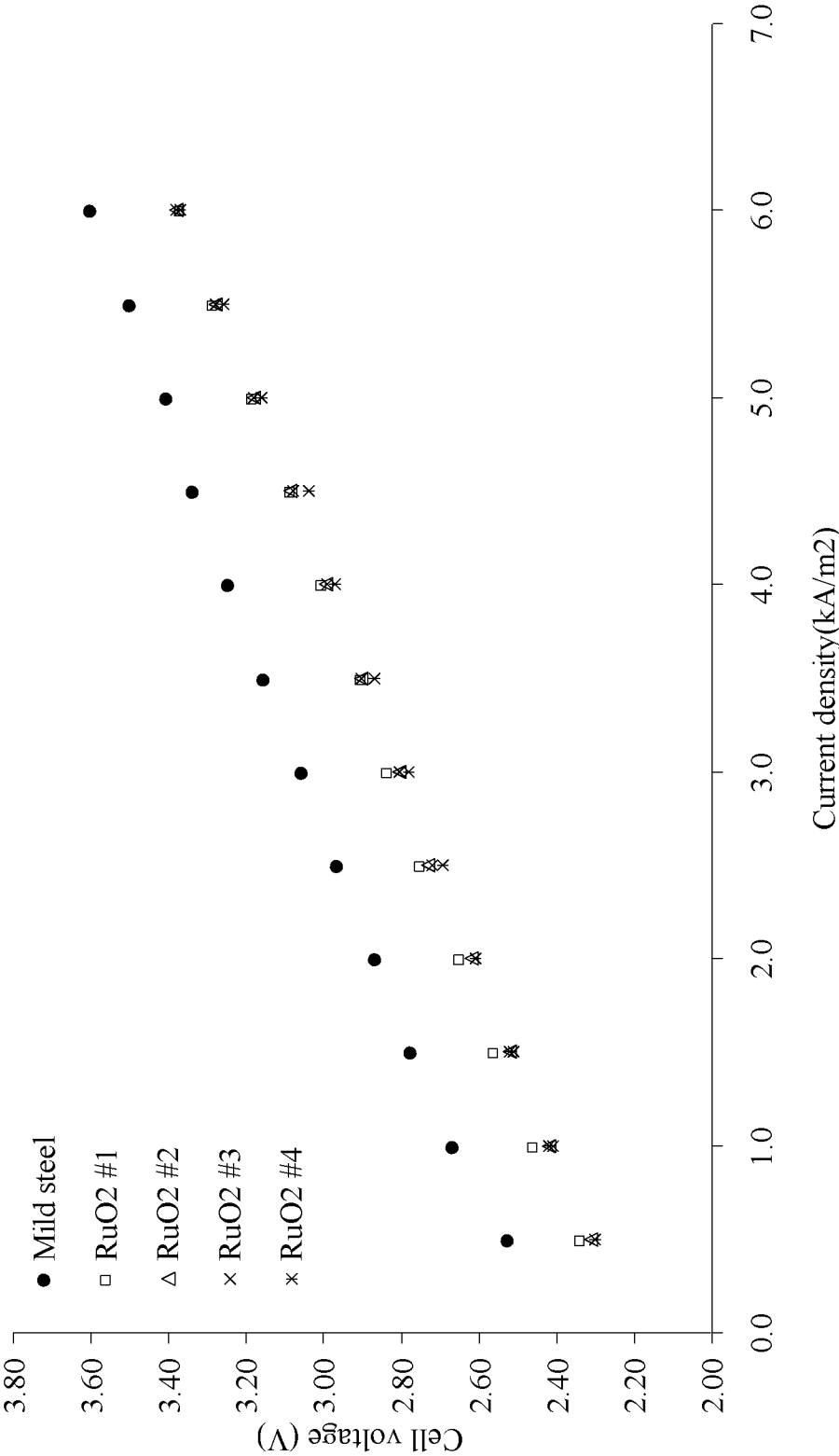


FIG. 3

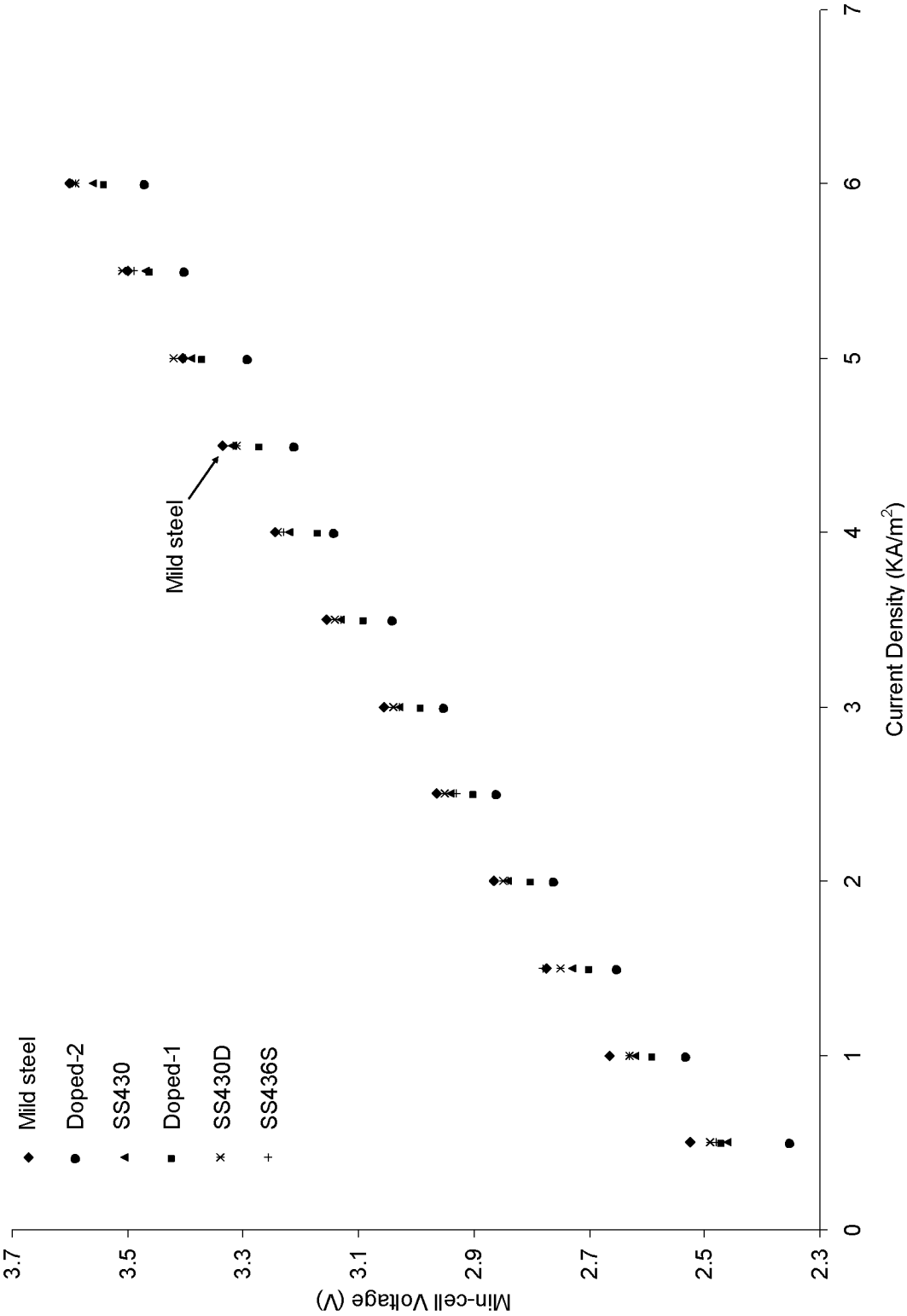


FIG. 4

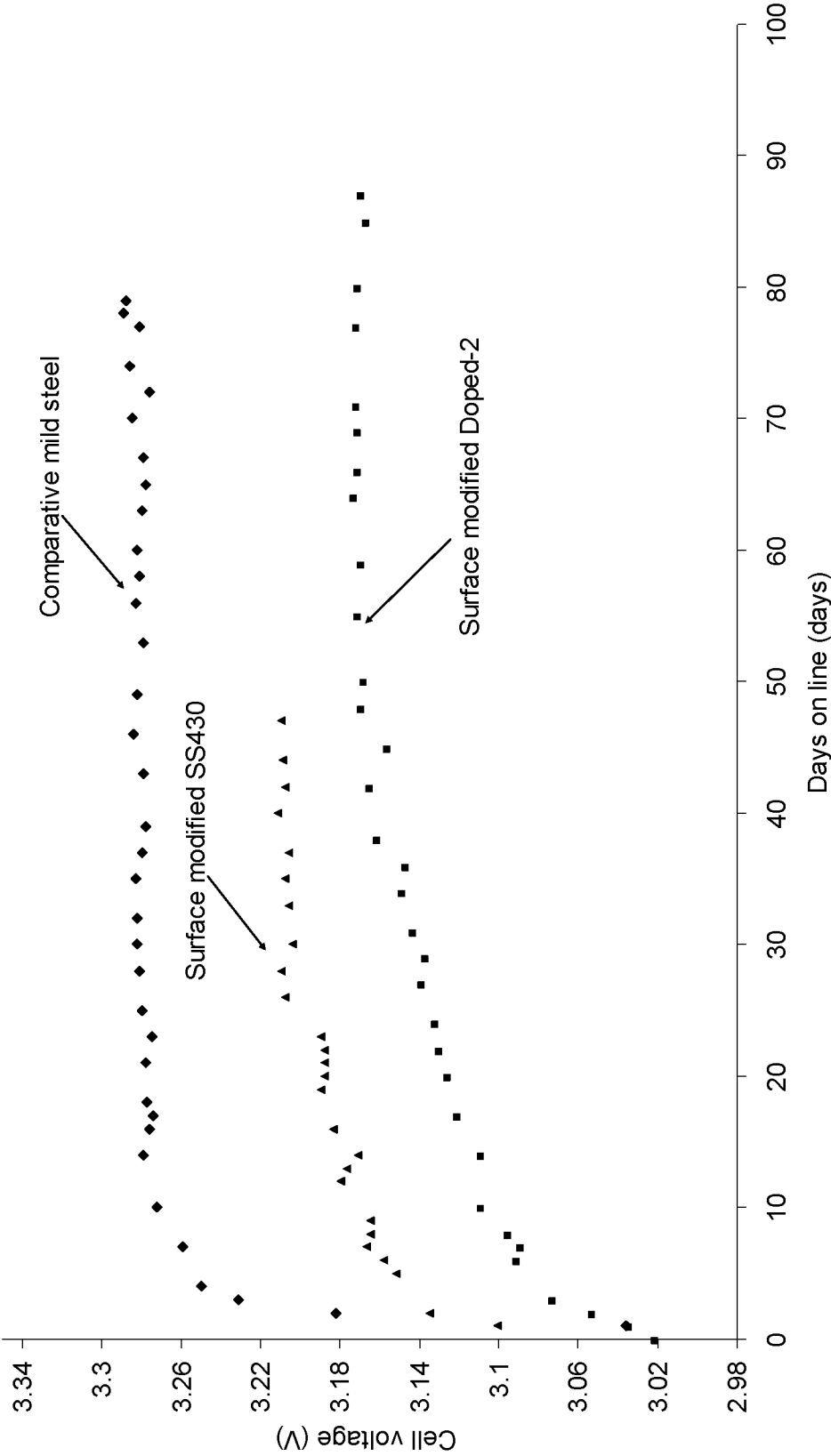


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2013/050289

A. CLASSIFICATION OF SUBJECT MATTER IPC: C25B 11/04 (2006.01) , C25B 1/26 (2006.01) According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC: C25B (2006.01)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) Total Patent, Canadian Patent Database, Scopus		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 8,133,366 (WEBB) 13 March 2012 (13-03-2012) *Columns 4-6*	1, 2, 10 and 16 11 and 12
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents :	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	
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"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 10 May 2013 (10.05.2013)		Date of mailing of the international search report 14 May 2013 (14-05-2013)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476		Authorized officer Chris Bowen (819) 994-3555

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2013/050289

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US8133366B2	13 March 2012 (13-03-2012)	AP200704158D0 AP2293A AU2006222554A1 AU2006222554B2 BRPI0607476A2 CA2600645A1 CN101166850A EA200701927A1 EA011667B1 EP1866461A1 EP1866461A4 JP2008533296A JP2012211397A KR20070119663A MX2007011014A US2006201586A1 US7807028B2 US2008095655A1 US7807029B2 US2010314255A1 WO2006094355A1 ZA200707954A	31 October 2007 (31-10-2007) 31 October 2011 (31-10-2011) 14 September 2006 (14-09-2006) 11 December 2008 (11-12-2008) 08 September 2009 (08-09-2009) 14 September 2006 (14-09-2006) 23 April 2008 (23-04-2008) 28 April 2008 (28-04-2008) 28 April 2009 (28-04-2009) 19 December 2007 (19-12-2007) 11 February 2009 (11-02-2009) 21 August 2008 (21-08-2008) 01 November 2012 (01-11-2012) 20 December 2007 (20-12-2007) 25 February 2008 (25-02-2008) 14 September 2006 (14-09-2006) 05 October 2010 (05-10-2010) 24 April 2008 (24-04-2008) 05 October 2010 (05-10-2010) 16 December 2010 (16-12-2010) 14 September 2006 (14-09-2006) 27 May 2009 (27-05-2009)