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MODELLING AND MEASUREMENTS ON A DEVICE FOR CURRENT FOCUSING IN AN ELECTROLYTIC PROCESS

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Abstract An electrical model of ionic current distribution in electrolytic solutions, in asymmetrical geometry of electrodes, is proposed. The results are compared with the known ones carried out by a software specialised in symmetrical current flow computing. By means a systematic campaign of computing, the electrical and geometrical parameters of a ionic current focusing device are found. A computer controlled experimental apparatus, based on such parameters, is also presented. Early measurements on this device seem to confirm the model validity.

Keywords: Electrolytic current focusing, Current flow modelling, Historical artefacts restoring.

1. INTRODUCTION

The problem of restoring of historical metallic artefacts is very important. In 30's the British Museum Laboratories proposed a process, utilizing an electrolytic solution with the artefact as cathode, to cause the inversion of its oxidation [1]. In the last years of the past century French and Italian restorers tried to apply this method, originally quite rough, to little objects with high density of superficial information, like coins or seals [2]. This involves some problems because the reduction current on the artefact's surface has a density depending on the local oxidation crust thickness, being the oxides intrinsically low conductive materials. This makes reduction not uniform, but above all, local high current density develops volatile hydrogen, caused by the connected water hydrolysis, that may locally strip oxidation crust, definitively damaging the artefact. A solution is to restrict the ionic current to a circumscribed area (focusing) and scanning the whole artefact's surface, thus strictly controlling the reduction process.

As shown in Fig. 1, focusing electrode sinks the peripheral part of the reducing current I_a, leaving its central part to reach the faced area of the cathode. Focusing degree depends on a number of parameters: the ratio F between I_f and I_a, the radius r of ring with respect the anode-cathode distance, the distance z between ring and cathode, the cathode's dimension etc. Studying the behaviour of such a device by means an analytical handling in three dimensional space becomes very hard, thus an electrical model of the electrolytic cell has been chosen.

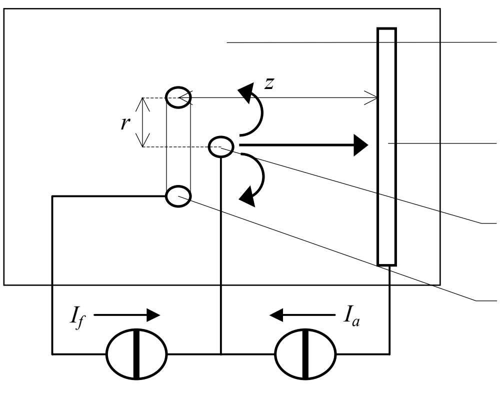

Fig. 1. Schematic focusing device.

2. A REALLY VIRTUAL MEASUREMENT

This method lends itself to a kind of application that may be really called "virtual" [3]. Measuring a certain number of observable parameters (the paper will show the method), values of local electrical parameters of the crust otherwise not accessible can be extracted. These are very important for archaeologists and restorers whose target is strictly control the reduction process acting on current, focusing and application time for each point of artefact's surface.

3. MODELLING

Taking into account that a constant generator forces its current independently by the electrochemical potential developed by metallic electrodes and that the conductivity of a solution is isotropic, an isotropic cubic cell formed by six resistors connecting a central node with the surrounding

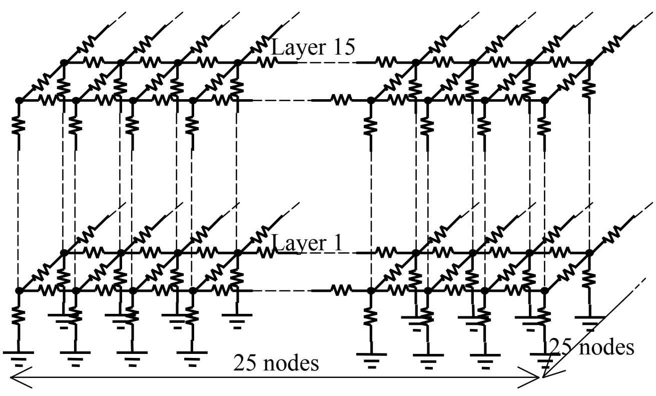

Fig. 2. Electric model of the electrolytic solution.

faces may represent an elementary volume of solution. An electric model of a parallelepiped containing an electrolytic solution is built arranging a number of cubic cells in a plane layer and superimposing a number of layers. In this paper is discussed a model with 15 layers of 25x25 cubes (nodes), shown in Fig. 2. The cathode is carried out by connecting to ground all the lowest resistors (625) in the first layer. The anode is the central node in layer 10, lying on vertical symmetry axis, connected to ground through the current generator I_a**.** The focusing electrode is approximated using a number of nodes depending on the wanted radius *r*, forming a polygon that simulates a ring, axial with anode's node, and lying on the layer *z* from cathode. To preserve their individuality those nodes are connected to the current generator I_f through an equal number of null voltage generators. The whole structure consists in 9376 nodes, 27375 resistors, 2 current generators and a certain number of null voltage generators, depending on ring's radius. Determining current density distribution means computing the "operating point" or static condition of the whole circuit by means a circuit simulator and take into account voltages of the 625 nodes of the first layer. This structure was composed by an appropriate software in Spice-text form and computed by MicroCap™ 5. On a 300 MHz CPU with a 256 Mb RAM computing time is about 22 minutes, over all depending on RAM access speed.

4. MODEL EVOLUTION

Current flow computing software, like QuickField™ 4, can get a current density distribution in a few seconds; unfortunately it works in axisymmetric geometry (a cylindrical volume) whereas the final target was to evaluate current distribution scanning the whole surface (asymmetric geometry). Nevertheless present paper tries to identify the geometrical parameters for a focusing device and the axial symmetry is suitable. Must be noted that in the circuital model, elementary cubes located on the boundary are debarred of a resistor (and more than one on the edges), that means the solution is closed in a non-conductive container. To enlarge boundary conditions without prohibitive time growing, the equivalent resistance, seen by a generator located in the central node of every layer, was computed. Fifteen different resistance values were found (one for every layer) and added to terminate to ground each node of each layer's boundary. This enhances of 1440 resistors the model and leads computing time up to 28', but is equivalent to double its base size (see Fig. 3). Computing by means

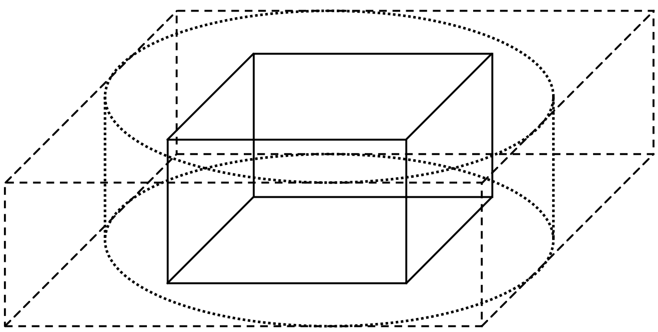

Fig. 3. Comparison among model volumes.

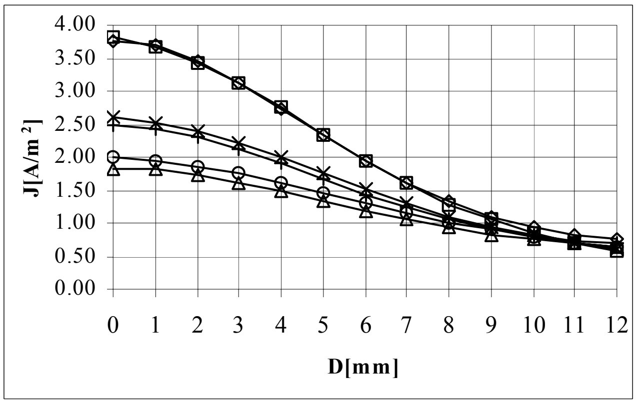

Fig. 4. Current density vs. displacement from symmetry axis, by QuickField™ (□, ×, ○) and by MicroCap™ (◊, +, Δ), for tree focusing ratios F=0, F=1, F=3.

QuickField™ 4 current density distribution in a compatible volume of conductive material, gives results in satisfying agreement with those carried out with the modified model.

For making compatible the results from the different ways of computing, circuital model is set considering 1mm the distance among nodes, 25Ω the elementary resistance, 1mA the current generator I_a and I_f as required by focusing ratio *F*. In Fig. 4 distributions are shown for tree ratios I_f / I_a, using a ring's radius r = 5mm at level z =12mm. Differences may be noted between curves specially for $F = 0$ (about 6.5%) and $F = 1$ (about 2.1%), probably due to different base area between computing systems (Fig. 3).

5. COMPUTING CAMPAIGN

The less time expensive QuickField™ (in its educational version) has permitted to face out a systematic campaign in current density distribution computing as function of ring's radius ($0 \le r \le 13$mm), of ring's height ($5 \le z \le 15$mm) and focusing ratio ($F = 1$ and $F = 3$), being the anode position fixed to 10mm. In Fig. 5 a three dimensional graph gives a synthesis of the results. Axial current density is represented vs. *r* and *z*, this generates two (intersecting) surfaces. It may be noted that a focusing ring nearer to the cathode than the anode (z < 10mm) with a radius r < 5mm sinks current from cathode (unsuitable for our purpose). On the other hand a larger radius (r > 10mm) works well in every position, but resulting awkward. A better solution seems a ring reduced to a little sphere ($r = 0$) in a far position (z = 15mm), that has a limited loss in focusing power with respect to larger radii.

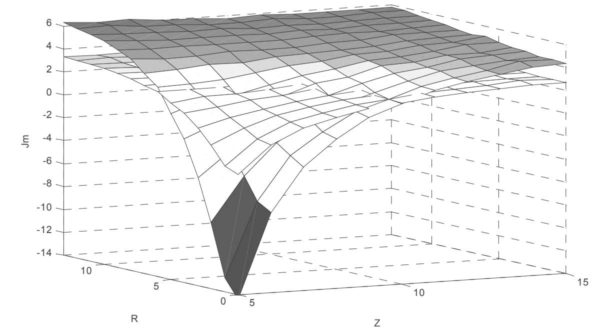

Fig. 5. Axial current density vs. ring's radius and height

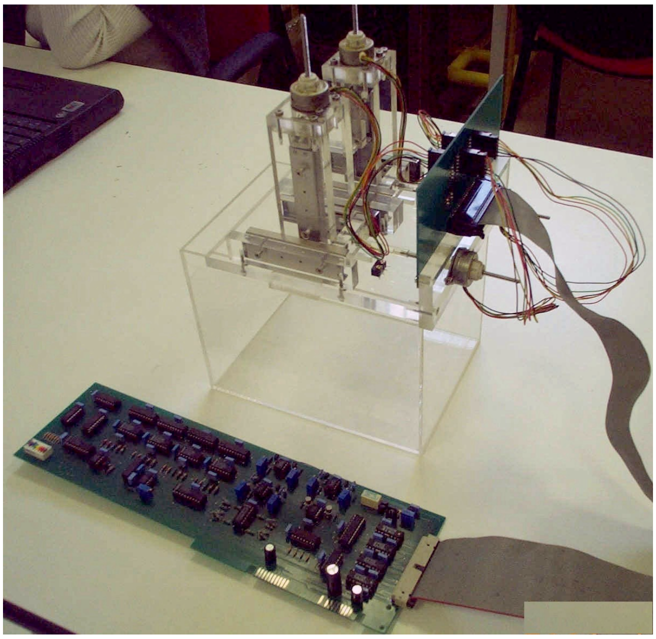

Fig. 6. Photograph of the experimental apparatus

6. EXPERIMENTAL APPARATUS

A prototype of an apparatus for automatic reducing of metallic artefacts has been designed and built up by our team (see Fig. 6). Such an apparatus must be equipped with two focusing devices, contemporary reducing both artefact's sides (recto and verso), moved vertically and horizontally on a certain path for scanning the whole surface.

The tank containing the electrolytic solution, the artefact's holder and the structure supporting moving parts was made in Plexiglas, material resistant in sulphuric acid solutions. Linear stepping actuators, moving on steel slides, drive the focusing electrodes.

An EISA-PC board contains the stepping motor drivers, the constant current generators, the analog-to-digital converters and the digital circuitry for communicating, through EISA BUS, with a personal computer.

The software, developed for this task in Visual Basic™, allows the focusing devices to follow independent paths on the artefact's sides, to control each reducing and focusing current and to sample anodes's and solution's potentials during the process. It also elaborates the sampled potentials to extract local electrical parameters, correlated with the reduction state, for modifying the process.

Such a versatile apparatus lends itself, with limited modifications, to the purpose of validating the proposed electrical model by means a measurements campaign on focusing devices using different geometries.

Measuring a microampere magnitude current in an acid electrolytic volume is not quite an easy goal.

As for anode and focusing ring also the target (cathode) must be resistant in a sulphuric acid solution. Thus a single face gold plated copper printing circuit board, 100mm in width and 150mm in length, has been chosen. A gloss insulated copper wire (ϕ = 1.1mm), whose end was gold plated, has been put in a hole of opportune diameter opened in the middle of the board with the role of current collector (Fig. 7).

In a target large enough to avoid undesirable edge effects, has been so created a little area (about 0.95mm^2) collecting a current *I(d)* associated to its displacement *d* from the axis of the focusing device. Measuring these currents in a range of displacements from 0 to 25mm (i.e. in horizontal), being such a phenomenon cylindrically symmetric, means to reconstruct the whole current density distribution (Fig. 8).

Converting current in voltage, due the need of the analog-to-digital conversion, involves the use of an operational amplifier. Care must be taken selecting this device. Not only it must present extremely low input bias current, but it must offer a very low offset voltage: in the converter circuit any output offset takes away the inverting input from its virtual ground value

Although the reducing current, sourced by a constant generator, is insensitive to electrochemical potentials developed near the cathode, any potential of the current collector different from the ones of the surrounding target (ground) may introduce an enhancement or an impoverishment in the current, misrepresenting its value.

Op Amp CMOS technology offers a large choice of devices with adequate input bias current and low offset voltage (i.e. for LMC6061A, typically 10fA and 100µV), but the experience shows that an offset null circuit applied to the non inverting input is needed.

Following the results of computing campaign, six kind of geometries in focusing devices has been adopted: three focusing rings with radius r = 10mm, r = 5mm and r = 0mm (a little sphere equal to anode one, with 1mm in diameter) each posed at two distances z = 12mm and z = 15mm.

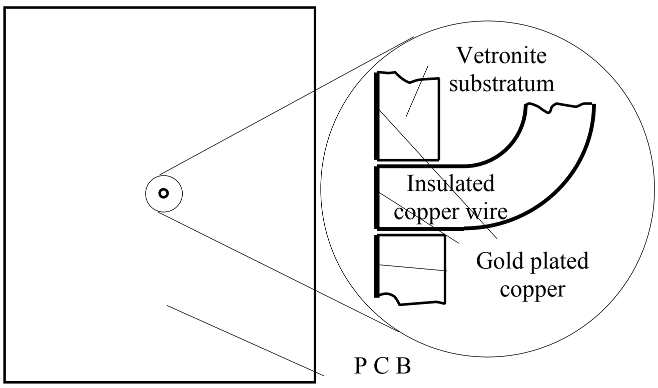

Fig. 7. The target and a detail of it's current collector

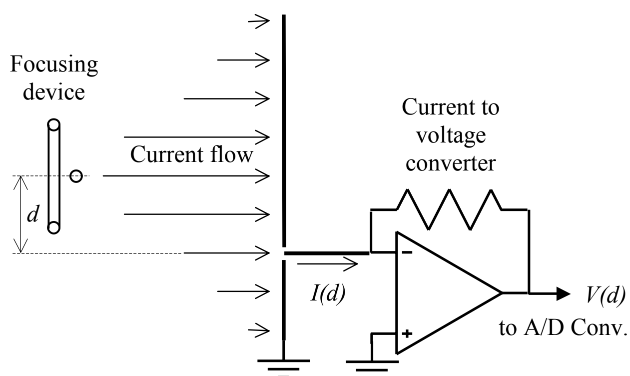

Fig. 8. Schematic current collector circuitry

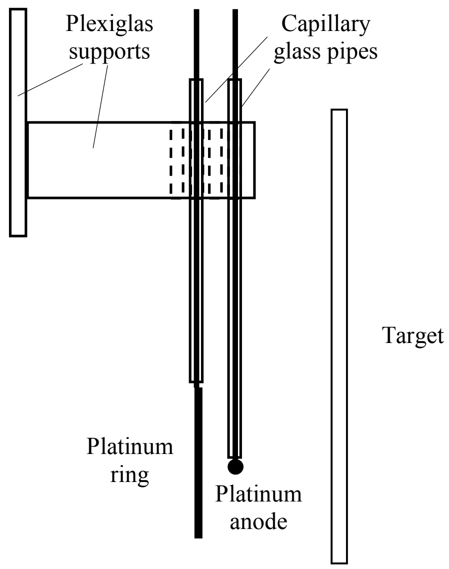

Fig. 9. An example of practical focusing device

As shown in Fig. 9, electrodes were carried out using a platinum wire (ϕ = 0.5mm) inserted in a capillary glass pipe (external diameter about 1.4mm) sealed off using an acid resistant glue. Glass pipes are inserted in calibrated holes opened in a Plexiglas support; it is glued to a Plexiglas stick gazed at the vertical iron slide.

7. CONCLUSION AND PERSPECTIVE

Although presently the measurement campaign is yet in progress, some reflections may be already done.

Two significant limits affect the proposed electrical model: 1) a continuous ring electrode is simulated by a finite number of nodes disposed on a polygon (i.e. for r = 5mm, 28 nodes on an octagon); 2) a well larger volume of electrolyte is involved in real experience with respect to the one of the electrical model, because of prohibitive computing time.

On the other hand the aim of this work is to reach qualitative answers about the behaviour of current distribution for a certain focusing device, rather then an accurate agreement between computed and measured values.

An other task is to avoid a mechanical movement of electrodes for scanning the artefact's surfaces. In fact it is thinkable to cut the ring in three or four sections each supplied by its own current generator. Administrating these components of the focusing current, it may carry out a displacement of the focusing phenomenon with respect to symmetry axis of the electrodes' structure. This work tries to validate a model, fundamental for studying such a development.

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