Ion cumulation by conical cathode electrolysis and ultrahigh pressure generation.

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Full version

Abstract The interionic force amplification along conical cathode slopes takes place during solid-state electrolysis. Both electric measurement and conical samples destruction corroborate it. Any limits of the ion cumulation have not been found so far. The effect is suited for ultrahigh pressure generation.

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1. Introduction

The investigation concerns ultrahigh pressure generation. Standard high pressure technology methods (such as Bridgman or diamond anvils [1]) use mechanical equipment carrying out concentration of a outer load into a very small area. A needle makes something like, although the anvils geometry is quite different. The methods, developing several Mbar pressure to date, lead to only 20-30% material volume decrease. None of laboratories have opportunity of ten or hundred times static reduction of an interatomic distance even over a microscopic area. Couples of particles collide by accelerators for only very short time. Astronomical objects (Earth's core, white dwarfs) alone condense a matter to such level. Even two times permanent reduction of interdeuterium distance (in D_2 molecule) should lead to considerable rate of pycnonuclear fusion reaction [2] that could mark the pressure

achievement. Standard high pressure technology tasks (metallic hydrogen, and other phase transitions) are relevant to this investigation.

In electrochemical field, a big pressure generation was suggested in course of dendrite propagation through a electrolyte crystal [3,4]. Quite different mechanism of ion focusing within an wide flat crack filled with sodium was under consideration there. Macroscopic mechanical action of an ion current was analysed also [5]. But flat electrodes of the samples ruled out any attempts to cumulate the stress appeared near the inert cathode.

Now reasons for a completely non-mechanical method of the pressure generation will be shown. The conical sample (fig.1) demonstrates basic idea of the



Fig 1,2. The samples under consideration: 1 – electrolyte, 2 – Al-foil anode, 3 – cathode. The crack through the most thick electrolyte layer demonstrates the stress concentration compared with cone foundation area.

method. In fact, it is Bridgman anvils without any moving parts, where instead of the outer mechanical load an electrochemical force produces a stress near the cone

foundation that amplifies along cone slope. Although the idea seems very simple neither the cumulation presence nor its absence could be proven theoretically. For example, the forces could be diffused by microrelief of the cathode surface that would transfer the initial load to bulk of electrolyte. As it will be clear below the Nature helps us at the point and the surface refines itself even without previous polish. Other theoretical questions about a force balance between ions and crystal lattice had been pointed out earlier [6].

2. Corroboration of pressure amplification.

Electrolysis of conical (fig.1) and cylindrical (fig.2) samples were compared. Sodium (Na^+) ions are moved through the electrolyte and received on cathode surface. When the surface will be saturated by the ions the current will cease. But even in course of first electrolysis, full charge passing through conical sample was about 2 times of cylindrical one (about 0.05 C) although the areas of both cathodes covered by electrolyte are equal.

Then the electrolyte was replaced by native one. Cylindrical sample results did not change upon it, but both conductance and full charge through conical sample increased because of the mentioned self-polish of cathode surface during first electrolysis. On third electrolysis an electrolyte destruction starts. Character of the destruction depends on temperature level that defines whether the electrolyte is brittle or plastic. In the brittle case the crack appears (fig.1), and current ceases soon like the cylindrical sample result because the cumulation pattern disappears at the destruction moment.

Plastic deformation counterparts are very big conductance and full charge. Stress developed in course of the plastic deformation is limited and this regime should be avoided. So the brittle state of electrolyte is preferable. To date the experiments were repeated with more small cathodes down to 0.2 mm in diameter. The electrolyte dimensions are not changed, and strength of the samples should be much bigger. Nevertheless, the above results are repeated again except the crack character. Now "the crack" come to the electrolyte surface as a spot or strip of multibubble porosity.

The mentioned practical appointments of the effect require more strength and brittle ion-conducting substances such as β -alumina and thin cathodes. The pressure should not be limited here.

3. Experimental details.

The details are not relevant to the method essence and should not take place in experiments with other electrolytes.

As ion-conducting substance (1) the sodium stearate ($C_{17}H_{35}COONa$) was employed. Its melting point is 250°C and at about 180°C the substance provides 0.05-0.1mA Na⁺ current through the native samples. Anion current is impossible (long hydrocarbon tail). Na cannot leak to atmosphere and diffuse through electrodes (as hydrogen could do). The substance is strength enough and brittle that usually prevent plastic deformations of the samples. Electron conductivity of the substance is zero.

Surfaces of the steel cathodes were ground to give an white metal finish, and cleaned by spirit. Accuracy of the conical tip was about 0.2 mm. Equal areas of the both cathodes were covered by electrolyte in course of its melt crystallization. Heat of the crystallization was transferred into the electrodes that defined the outer surface shape. Small heat-conductivity of sodium stearate limited electrolyte layer thickness above the steel surfaces. It is the only technological problem of the investigation.

Between the two electrolysis processes the conical cathode was cleaned without any abrasives to save the surface state appeared in course of its ion refining.

Temperature level control was realised by sample initial conductivity measurement. So for the brittle destruction regime appearance the temperature was decreased until refined sample current would be the native sample level (0.05-0.1mA).

The crack pointed out in fig.1 directs along sample axis that means transversal character of the stress developed inside the electrolyte. A conical sample dielectric crack appeared also after first and second electrolysis, but it took place during several days storing at room temperature. The crack position was usually near cathode cone foundation.

4. Conclusion.

These experiments proved existence of the interionic force amplification mechanism and exhausted the strength opportunity of the solid electrolyte used. So there is necessity to continue the investigation with usual superionic conductors. They possess both the high mechanical strength and ion conductivity.

References

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Another keywords: polarization, depolarization, ionic conductor, superionic conductor, ice, crystal, strain, V-center, V-centre, doped crystal, interstitial impurity, intrinsic color center, high pressure technology, Bridgman anvil, experiment, crowdion, dielectric, proton, layer, defect, lattice, dynamics, electromigration, mobility, muon catalysis, concentration, doping, dopant, conductivity, pycnonuclear reaction, permittivity, dielectric constant, point defects, interstitials, polarizability, imperfection, defect centers, glass, epitaxy, sodium hydroxide, metallic substrate, melt, crystallization, point, tip, susceptibility, ferroelectric, ordering, force, correlation, collective, shift, distortion, coalescence, crowdions, electrolysis, cone, slope, slopes, glass.

An experimental result: Ice SuperPolarization. < http://to2084.narod.ru/index.html#exp>

Questions and answers. <http://to2084.narod.ru/Question.htm>

Numerical simulation results. http://to2084.narod.ru/Simul.htm

Long-time-current experimental result with conical cathode: <u>Part I.</u> http://to2084.narod.ru/Cone2.htm <u>Part II.</u> NEW http://to2084.narod.ru/Cone2.htm