

higher taxon of the Bivalvia. The Lucinacea are probably unrelated to most other "heterodont" bivalves with which they are commonly associated because of vaguely similar patterns of dentition.

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Electrolytic Growth of Silver Dendrites

Abstract. The growth rates of silver dendrites formed in narrow capillaries by electrodeposition under various physical conditions have been determined. Dissolution of such dendrites as well as their growth can be reliably controlled. This principle may be used in the design of components for adaptive electronic systems.

The formation of dendrites occurs in many modes of crystal growth, but the phenomenon appears to have been studied relatively little, owing to the complexity of the situation and to the lack of an experimental approach which enabled quantitative investigations to be made. Theories of the formation of dendrites from dilute solutions have been advanced by Papapetrou (1) and by Seeger (2), and Saratovkin (3) has considered dendritic growth from a melt. Silver dendrites formed by electrolytic processes have been described by Fischer, Wranglen, Yang, *et al.*, and by Faust and John (4).

In an electrolytic cell in which a metal is being deposited, each ion arriving at the cathode can either be added

to one of the crystals already present or it can form the nucleus of a new crystal. The physical conditions in the cell determine which of these situations is more likely to occur. If ions are added to existing crystals, a few large crystals will be formed. If ions form nuclei of new crystals, a conglomeration of small crystals will result. Sometimes the large crystals grow outward from the cathode and form dendritic structures.

A number of factors influence the type of deposit, the most important being the presence or absence of inhibitors, the current density, and electrolyte concentration. Inhibitors are substances or conditions which reduce the tendency for crystals to grow and which generally discourage the formation of dendrites. The form of some deposits, however, has been attributed to the presence of inhibitors through selective action on different crystal faces (5).

The effects of current density and electrolyte concentration are in many ways complementary. In a cell in which inhibition is slight the tendency is for crystals to grow into regions where the metal ion concentration is greatest. If the electrolyte concentration is small, as the current is raised the ions in the neighborhood of the cathode will rapidly be removed, and the crystals will grow outward to the richer regions. If the electrolyte concentration is greater, it is possible to raise the current to a greater level before the cathodic regions become depleted in metal ions and dendritic crystals are formed.

Most investigators have postulated a number of crystal types and then determined the type of crystal which grows under given conditions (6). This approach is quite satisfactory for small crystals, but with increase in crystal size (greater than 1 mm in length) the crystal "type" becomes a continuous, rather than a discrete, quantity so that the "types" chosen are to some extent arbitrary.

As the crystals grow in an unrestricted electrolyte they alter the electrical field and ionic concentration distribution in their own neighborhood, and thus change the conditions which influence their growth. The dynamics of crystal formation cannot be studied.

If the cathode of a cell connects with the main compartment (containing the anode) only by way of a narrow channel such as a capillary tube, any crystal growth which occurs must take place along this channel (Fig. 1). If the cur-



Fig. 1. Dendritic growth in a capillary tube.

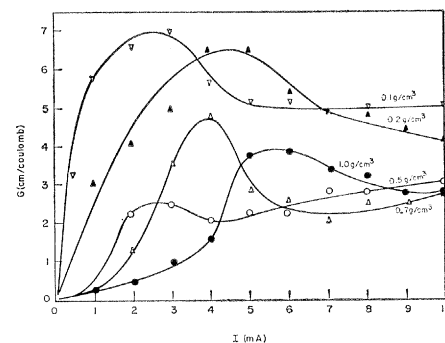


Fig. 2. Axial growth rate per unit current (G) versus current (I) for silver dendrites grown in electrolytes containing various concentrations of silver nitrate. The capillary tube had a diameter of 1 mm.

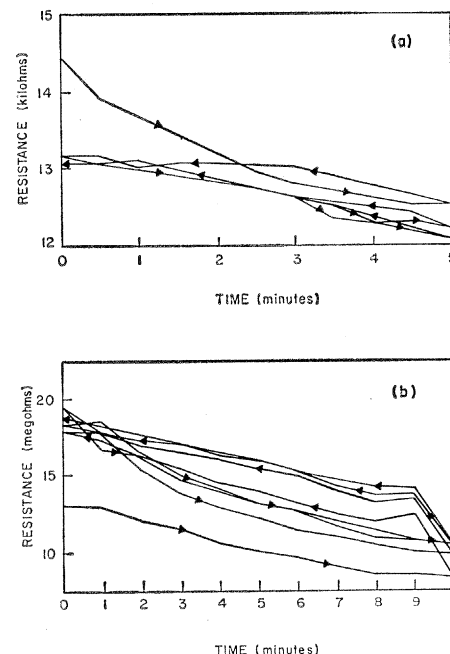


Fig. 3. Reversible growth and dissolution of silver dendrites. *a*, Concentration 1.0 g/cm³, 4.0 ma; *b*, concentration 0.1 g/cm³, 0.1 ma. The incomplete dissolution of the dendrite shows itself in *a*. After the initial growth of the dendrite, the range of resistance change is reduced by small pieces of silver remaining in the tube. These sometimes become incorporated in new dendrites. The "loops" in *b* are thought to be due to polarization.

rent is kept constant a state is rapidly attained in which conditions at the growing tip remain the same.

If q coulombs of charge are passed through the cell, and if the current through the cell consists entirely of the transport of metal ions, and if a metallic dendrite of mean cross-section $\bar{a}$ (cm²) is formed, its length x will be:

$$x = \frac{eq}{F\rho\bar{a}} \quad (1)$$

where e is the chemical equivalent of the metal, ρ its density, and F is the Faraday (96,500 coul).

A current of I amperes will cause the dendrite to grow at a rate

$$\frac{dx}{dt} = \frac{eI}{F\rho\bar{a}} \quad (2)$$

If the cathode is connected to the anode by way of a tube of uniform cross-section a (cm²) and length x_0 (cm), filled with electrolyte of conductivity σ (mho cm⁻¹), the resistance of the cell will then be

$$R = R_0 + \frac{x_0 - x}{\sigma a} \quad (3)$$

where R_0 is the resistance of the rest of the cell excluding the tube. The rate of change of resistance of the cell when a current I flows through it is

$$\frac{dR}{dt} = -\frac{1}{a\sigma} \frac{dx}{dt} = -\frac{eI}{F\rho\sigma a\bar{a}} \quad (4)$$

Equation 2 can be rewritten in order to yield a quantity which can be measured. We define a quantity G which expresses the increase in the length of the dendrite in centimeters when 1 coul of charge is passed through the cell:

$$G = \frac{1}{I} \frac{dx}{dt} = \frac{e}{F\rho\bar{a}} \quad (5)$$

Since this quantity depends upon the mean cross-section of the dendrite, the value of G may be taken as a continuous measure of the "type" of dendrite.

Figure 2 shows G as a function of current and concentration for the growth of silver dendrites in a cell containing silver nitrate electrolyte and silver electrodes. For an electrolyte of given concentration, the transition point between the type of crystal which almost fills the tube (formed by relatively low currents) and the true dendritic type is quite sharp. The current at which this point occurs is greater for higher concentrations, agreeing with the qualitative considerations discussed earlier.

The peculiar electrical and geometrical properties of a narrow tube filled

with an electrolyte permit not only the controlled growth of metallic dendrites, but also their controlled dissolution. The dendrites do not dissolve entirely; small pieces break off and fall to the bottom of the tube. Nevertheless, the resistance of the tube does change fairly smoothly (Fig. 3). This contrasts with the dissolution of dendrites grown in unrestricted electrolytes where the resistance of the cell often changes instantaneously to its maximum value.

The curves of Fig. 3 were obtained by measuring the resistance of the cell as a function of time while the current was passed in one direction for a given amount of time, then reversed for the same amount of time. After about five reversals the process stabilizes, and the resistance goes through reproducible cycles.

A need has been felt by the designer of adaptive machinery for a small, inexpensive component whose electrical properties can be adjusted automatically (7). It is possible that electrochemical cells of the design of Fig. 1 may fulfill this need (8).

The linear variation of resistance with time, coupled with the possibility of resistance changes in either direction, make these cells particularly attractive. The resistance of a cell can be "read" nondestructively with an a-c signal.

Cells with tubes about 1 mm in diameter and about 10 cm long have resistances of 1 to 100 kohm, which makes them suitable for incorporation into conventional electronic circuits. With these dimensions the time required for a reasonable change in resistance is of the order of minutes, which may seem rather long. By reducing the physical dimensions of the capillaries, advantage may be taken of the rapid axial growth rate in narrow channels (8). Because the resistance range of the cell remains approximately the same as long as the ratio of length to cross section of the tube remains the same, miniaturization of this cell permits the design of quickly responding elements with appropriately matched impedances for use in large adaptive systems.

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Pressure-Induced Trapping Phenomenon in Silver Iodide

Abstract. *Observations of the optical properties and electrical conductivity of silver iodide at pressures between 2 and 4 kilobars are indicative of the formation of free silver (or silver and iodine) in this pressure range. On the basis of the sequence of events and the volume relations, this reaction could account for the smooth and reversible phase transformations of silver iodide in this pressure range. The phenomenon may be due to the trapping of an electron by the silver ion (in a thermally excited state) as a result of the distortion of the lattice under pressure.*

Observations of silver iodide under pressure in a diamond anvil high-pressure cell have led us to the conclusion that the compound is unstable with respect to silver, and perhaps iodine, near the transformation pressure, reported by Bridgman to be 3.0 kb (1). The following experiments provide evidence to support this view:

1) The shift of the absorption edge of silver iodide with pressure observed in this laboratory differs slightly from that reported by Slykhouse and Drickamer (2) in that the absorption edge near the transformation shifts from 22,000 cm⁻¹ all the way through the visible and infrared regions (to a value less than 650 cm⁻¹); this difference suggests the presence of metallic silver.

2) When silver iodide is observed in the diamond cell at an applied pressure of 3 kb, a diffuse black band