The Principles of the Solion

A NEW RANGE OF ELECTROCHEMICAL CONTROL DEVICES

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The current flowing in an electrical circuit has been controlled in the past primarily by the use of vacuum tubes in which the flow of electrons through space is controlled by the imposition of electric fields. Recently the transistor, in which electrons and "holes" move through a solid, has replaced or supplemented the vacuum tube in many of its functions. Still more recently, a technology has been developed which makes use of the principles of electrochemistry to yield a series of circuit control elements in which the charge carriers are ions rather than electrons, and in which the working medium is a solution of ions. These devices have therefore been named *solions*.

Since the velocitics of ion movement in solution are extremely low in comparison with electron velocities, solions are inherently low frequency devices (o to 1,000 cps). While this limitation to low frequency operation places solions at a disadvantage in so far as incorporation into present electronic circuitry is concerned, these devices possess distinct advantages over the previously used elements for application in this frequency range as they permit a decided reduction in circuit complexity. Another outstanding advantage of the solion units is the extremely low power level required for their operation, much less, for example, than that required to operate a comparable transistor system. This low power requirement makes it possible to operate complete solion circuits for very long periods (years) with small hearing aid type batteries.

In most solion units the electrochemical circuit consists of inert metal electrodes in contact with a reversible redox electrolyte

A new technique, based upon electro-chemical phenomena, has led to the development of the solion, the name given to a range of versatile detector and control devices that supplement both the thermionic valve and the transistor. Solions have special advantages at low potential owing to their extremely low power requirements and to the simplicity of the circuitry involved. This article outlines the principles underlying their design and development and the operating characteristics of a number of distinctly different types of solium. Generally, they comprise an electrolyte of iodine and potassium iodide, with platinum electrodes.

system. The electrodes are usually of platinum, and are not only inert to the electrochemical reactions but also to chemical attack by any corrosive reagents in solution. Many of the reversible redox systems listed in the table of standard electrode potentials may be used as the electrolyte system; those which have been studied for this application include iodine-iodide, bromine-bromide, ceric-cerous, ferric-ferrous, ferricyanide-ferrocyanide, and thallic-thallous. In general, however, the iodine-iodide system offers the best combination of properties, such as freedom from interfering reactions over the operating voltage range, solubility and stability in both water and some organic solvents, and in the ease with which the desired electrode reactions proceed.

In an aqueous or alcoholic solution of

iodine and potassium iodide, the iodine exists predominantly as tri-iodide ion, formed by the reaction:

$$I_2 + I^- \rightleftharpoons I_3^-, \; K_{eq} \sim 710 \qquad (1)$$
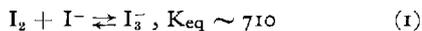
When current is passed through this solution, iodine will be reduced at the cathode to iodide ions, and the iodide will be oxidised at the anode to tri-iodide, as follows:

Cathode reaction: $I_3^- + 2e \rightarrow 3I^-$ (2)

Anode reaction: $3I^- - 2e \rightarrow I_3^-$ (3)
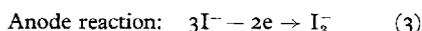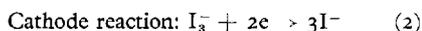
Thus there is no net change in the solution with the passage of current.

By using an anode of much larger surface area than the cathode, and an iodide concentration large with respect to that of iodine, the current becomes a function only of the rate at which iodine reaches the cathode, and the total voltage applied to the cell appears as cathode potential, E_c. This is one of the focal points in operation of the solion units, namely, that the current is controlled by conditions in the vicinity of the cathode only.

A typical plot of current against voltage is shown in Fig. 1 for solutions of three different concentrations of iodine. The current increases rapidly with voltage, obeying Ohm's law, until the supply of iodine to the cathode becomes limited, at which point the current
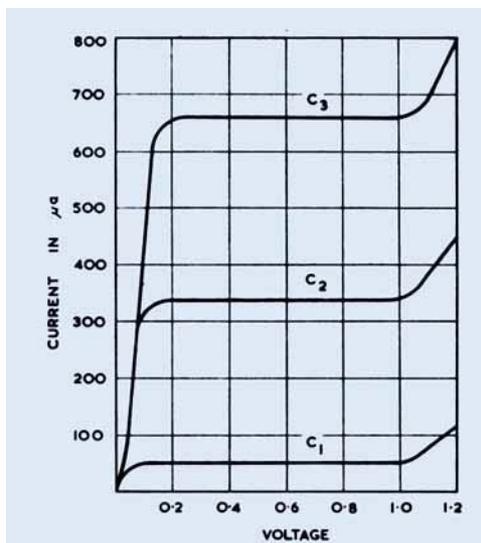

Fig. 1 *Typical relationships for current and voltage for solutions of three different concentrations of iodine*

levels out and becomes voltage independent. Since most of the potential drop appears at the cathode, each added increment of voltage makes the cathode a better reducing agent, so it is imperative to exclude from the solution all substances (other than iodine) which may be reduced over the operating voltage range. Oxygen, for instance, would be reduced at about 0.5 volt, lead at about 0.7 volt, etc. In
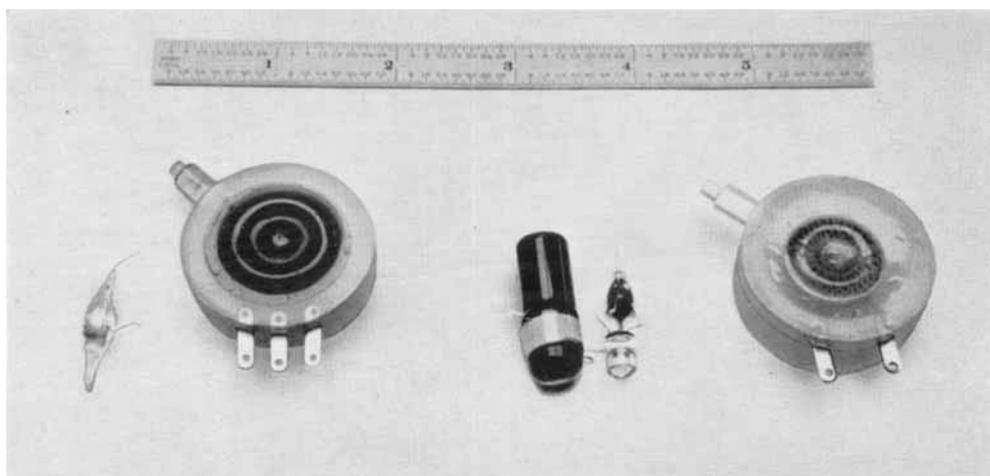

Fig. 2   *Solions may be of several different types. Those illustrated above are, from left to right, a diode, a detector, integrators and an electro-osmotic cell*
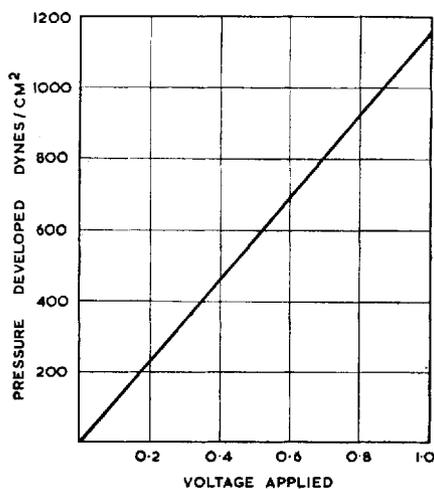
Fig. 3 Relationship between the pressure developed by a typical electro-osmotic cell and the applied voltage

Fig. 1 the second increase in current at about 1.0 volt is due to reduction of the hydrogen ions from the solvent; in solions this undesired side reaction is avoided by limiting the bias to 0.9 volt.

The value of the limiting diffusion currents of Fig. 1, for quiet, isothermal conditions, is given by

$$I = nFAD\left(\frac{dc}{dx}\right) \qquad (4)$$

where n is the number of electrons involved in the electrochemical reaction (in this case, two), F the value of the Faraday, A the cathode area, D the diffusion coefficient of iodine, and dc/dx the concentration gradient. Equation (4) and the phenomenon it describes, called concentration polarisation, are of utmost importance in the operation of most of the solions, since they make it possible to determine the concentration of iodine at any point in the solion by a simple electrical measurement, and to detect disturbances, such as flow, in the fluid.

In several of the solions, advantage is taken of the fact that iodine may be transferred from one region of a solution to another instantaneously by electrolysis, and that the amount so moved is an exact function of the quantity of electricity used (Faraday's law). Furthermore, the very large value of the Faraday makes it possible to obtain usable currents (microamperes) from the movement of extremely small quantities of iodine.

One other electrochemical phenomenon used in solion applications is that of electro-osmosis, which is the movement of a liquid through a porous medium, such as fritted glass, under the influence of a voltage gradient. Electro-osmosis is used in the solion units exclusively as a micropump to feed fluid flows into coupled units, and by selection of the right combination of disc sizes, porosities and working fluids, the magnitudes of voltages required and fluid flows developed can be made to correspond to those used and developed in the coupled units. In Fig. 3 the pressure developed by a typical electro-osmotic cell is plotted against the applied voltage. For additional details on
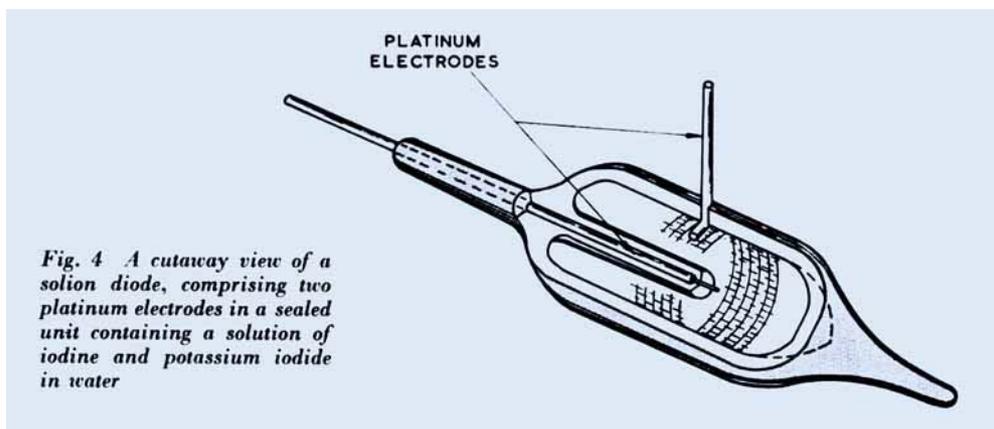

Fig. 4 A cutaway view of a solion diode, comprising two platinum electrodes in a sealed unit containing a solution of iodine and potassium iodide in water

the electrochemistry involved in solions, the reader is referred to previous publications (1, 2, 3).

Operating Characteristics of Typical Solion Units

At the present time there are several distinctly different types of solions which may be classified according to the function performed, as follows:

(1) Current limiter, or electrochemical diode

(2) Detectors, flow meters and transducers

(3) Electrochemical integrators

(4) Differentiators, multipliers and amplifiers

An idea of the general size and shape of typical operating units is given in the illustration on page 43.

The simplest solion is the electrochemical diode, which depends entirely on concentration polarisation for its action. Fig. 4 is a cutaway view of a solion diode, which simply comprises two platinum electrodes in a sealed unit containing a solution of iodine and potassium iodide in water. The polarisation curve for such a diode is given in Fig. 5, which shows the familiar rectifier characteristics, with a forward-to-reverse current ratio of about 500 to 1. Because of a storage charge effect inherent in the solion diode, it is not operable at frequencies above about 0.1 cps.

Solion detectors, flow meters and transducers take advantage of the increase in current resulting from the disturbance of the solution near the cathode. A schematic drawing of one type of detector is shown in Fig. 6; this detector incorporates essentially the same electrochemical circuit as the solion diode, but with a new geometry.

Here the cathode is in the form of an orifice through which the solution may be pumped by means of an external pressure incident on the plastic diaphragms. With no flow through the orifice, and with the electrodes biased at about 0.9 volt, a very small background current (a few microamperes) will flow in the external circuit. Forcing fluid through the orifice, however, disturbs the diffusion layer and causes the current to increase. The device thus produces a d.c. current which is a function of the amplitude of the flow. By suitable design of the detecting cathode, the functional nature of the response to flow may be varied; thus, elements with a linear, logarithmic, and square root response to flow have been built. The units are sensitive to flows down to 10^{-5} cm³/sec, or to incident pressures of a few dynes/cm². Units have been designed to detect and meter flows from d.c. up to some 200 cps.

The electrochemical integrator is probably one of the most important solion units, and is nothing more than the familiar iodine coulometer (4), but with some rather important changes in design. One type of integrator is shown in Fig. 7. It consists essentially of two separate electrolyte chambers, generally
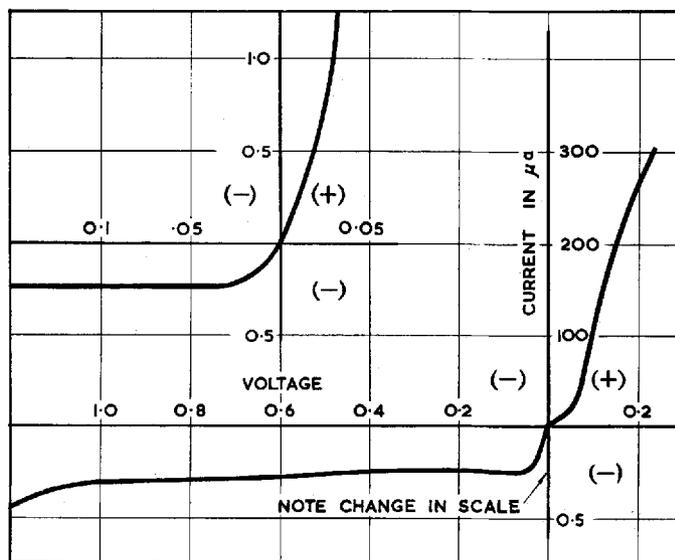

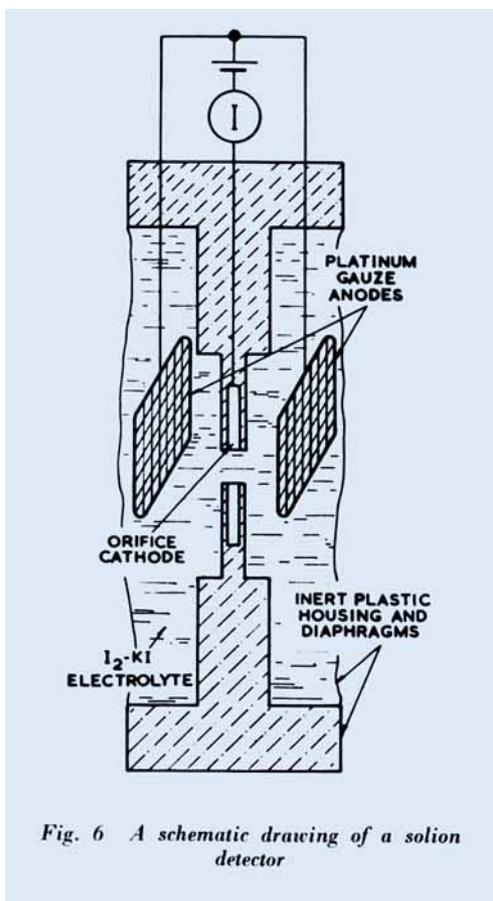*Fig. 5 A polarisation curve for a solion diode*

Fig. 6   A schematic drawing of a solion detector

iodine, and current is passed through the integrator in the direction shown in Fig. 7, the concentration of iodine in this chamber is proportional to $\int I dt$ at any time. Iodine concentration could be measured chemically, but as this would require disassembly of the integrator, it is usually measured visually by change in colour of the iodine solution, or electrically by measurement of the concentration voltage between the two compartments. Since the iodine-iodide system is electrochemically reversible, the integrator can be cleared or reset by passing current between the two electrodes in a direction opposite to the original integrated current.

Electrochemical Readout Integrators

Another type of electrochemical integrator is the electrical readout integrator (ERI).

In this type of unit, two electrodes are used to replace the "diffusion barrier" shown in the previous type. As the name implies, the integral value is determined by an electrical readout, the particular means being the limiting diffusion current. Since the limiting diffusion current is a linear function of the concentration, by imposing a voltage across the two electrodes in the integral compartment, one obtains a current which is a direct measure of the concentration. Since the volume is fixed, any change in concentration represents a change in the amount of reagent formed and hence a change in $\int I dt$. The integral values obtainable with this type of integrator are much smaller than the capacity of the type discussed previously. The ERI was designed, however, as a short-term integrator from which the integral value can be read within one second after integration is finished.

Differentiators and Multipliers

Solion differentiators, multipliers and amplifiers consist of the electro-osmotic cell coupled to solion detectors of various designs. Because of the very low frequency response of the electro-osmotic cell, all of these devices

of different volume, with a platinum electrode in each chamber, and filled with the iodine-potassium iodide electrolyte solution. Separating the two chambers is a "diffusion barrier", the purpose of which is to prevent mixing of the iodine in the two compartments, while at the same time maintaining a conduction path of electrolyte for the flow of current.

Faraday's law applied to this device may be expressed as:

$$\text{Grams of iodine formed at anode} = \frac{126.92}{96,500} \int I dt \quad (7)$$

where I is current in amperes and t is time in seconds.

Since the volume of the chambers is fixed, the concentration of iodine is directly proportional to grams of iodine in the chambers. Thus, if the small chamber is initially free of

operate from very low frequencies down to d.c. In the amplifier the solion detector operates linearly, and since the pressure developed by the electro-osmotic cell is linear with applied voltage (see Fig. 3) the output of the detector follows the input to the micropump, but with large current gains. The current and power gains obtainable by such a device may be illustrated by considering a detector which operates by reducing all the iodine contained in the fluid flowing past the cathode, which in this case consists of closely woven platinum gauze. The current output for this cell is given by:

$$I = 10^{-3} \; F \; N \frac{dv}{dt} \qquad (8)$$

where   F = 96,500
         N = normality of iodine in the fluid

$\frac{dv}{dt}$ = flow rate in cm^3/sec.

From this equation, assuming an iodine normality of 10^{-1}, flow rates of 10^{-5} to 10^{-3} cm^3/sec yield currents in the neighbourhood of 100 to 10,000 microamperes. Input to the micropump to drive the detector to 10^{-3} cm^3/sec is roughly 20–30 microamperes at 1.0 volt, which gives current and power gains of some 400-fold. It is in this manner that the large value of the Faraday, almost 10^5 coulombs/equivalent, makes so many of the solion units practical.

Differentiation and multiplication units are obtained by combining the electro-osmotic cell, detectors of various types, and hydraulic components such as bellows, resistive and inductive capillary tubes and capacitive diaphragms into complete hydraulic circuits
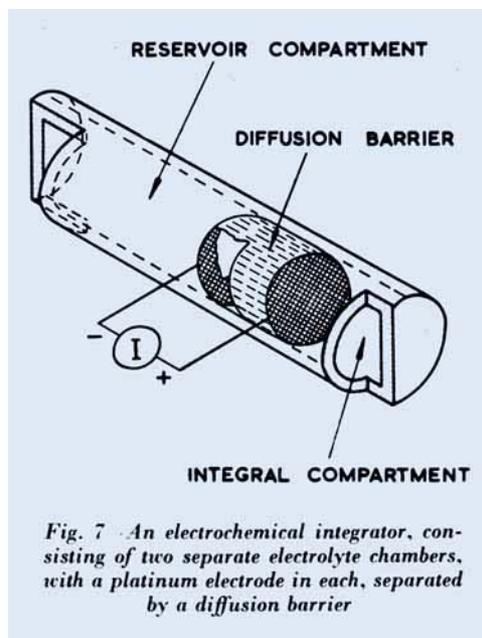

Fig. 7 An electrochemical integrator, consisting of two separate electrolyte chambers, with a platinum electrode in each, separated by a diffusion barrier

which are analogous to electrical networks.

Solion units other than those described here have been developed; still others are in the experimental stage. The technology of solions is young, having been developed over a period of about the last ten years. Many problems in design and fabrication remain to be solved; however, the basic theory is now well understood, and it is felt that solions will occupy an important position in the future of such things as control circuits and automation of chemical plants, where low frequency hydraulic measurements are common, in instrumentation, where long period differentiation and integration are often desired, and as components in almost any situation where low frequency hydraulic or electrical signals are available.

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