Electrochemical Supercapacitors as Versatile Energy Stores

POTENTIAL USE FOR PLATINUM METALS

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"Supercapacitors" are a new category of electrical condenser which are based on the properties of charge distribution at the interface of an electrode/electrolyte solution. After an introduction to the features of such devices, a brief history of their development is followed by a description of some technical details. The latter part of the paper is devoted to some specific properties of ruthenium and iridium oxides, RuO_x and IrO_x, which exhibit very interesting interfacial behaviour for their potential use in supercapacitors. In particular, these materials are very versatile in their method of preparation and in their surface properties. Prospects for changing the properties of the active layer of the superconductor by mixing two or more oxides are discussed.

Electrical energy is able to be stored either electrostatically in conventional capacitors, or electrochemically in cells or batteries (electrochemical power sources). For capacitors the electrical energy stored is given by:

$$W_{el} = Q\Delta V = C\Delta V^2 \qquad \text{(i)}$$

where ΔV is the electrical potential drop across the capacitor when electrical charge Q resides on its plates; C is the capacitance of the condenser defined as:

$$C = Q/\Delta V \qquad \text{(ii)}$$

The amount of charge Q, as well as the capacitance C, is directly proportional to the surface area of the plates. For ideal capacitors, C is a constant and Q and ΔV are linearly related, see Figure 1a. During charge and discharge electrical charges do not cross the capacitor but move in and out through the external circuit.

Batteries store and supply electrical energy through a quite different mechanism. Electrical energy is stored as the chemical energy of reactants which are then transformed at the interface of the two electrodes of an electrochemical cell. For instance the global reaction at electrodes PbO_2 and Pb of a lead-acid battery during discharge is:

$$PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O \qquad \text{(iii)}$$

Discharge takes place (ideally) at the V value fixed by the ΔG, the change in Gibbs energy, of Reaction (iii):

$$\Delta G = -nF\Delta V \qquad \text{(iv)}$$

where n is the amount of charge transferred for the transformation of a mole of reactants and F is the Faraday constant.

In principle, current is supplied by a battery at constant ΔV as long as active material is still available in the device, see Figure 1b. In terms of electrical concepts, its capacitance would thus be infinite. However, during charging and discharging electrical charges cross the electrode/solution interface so that this device behaves electrically more like a resistor than as a capacitor. Nevertheless, the amount of electrical energy stored can be calculated by also using Equation (i). Since Q is very large, W_{el} will be orders of magnitude higher than for conventional capacitors. However, the power density, that is, the power per unit volume or mass, will be orders of magnitude higher for conventional capacitors because of their smaller size. Moreover, the lifetime of batteries is limited by the number of charge/discharge cycles.

So-called double-layer or electrochemical capacitors fill the gap between the above two categories, see the Table overleaf (1, 2). Electrical energy can be permanently stored at the electrode/electrolyte interface due to the spontaneous charge separation occurring as the system attains electrostatic or electrochemical equilibrium. This is schematically shown in Figure 2. If the metal is negatively charged, for example, cations accumulate at the interface on the solution side at a distance of the order of magnitude of a few molecular diameters. In view of the high dielectric constant of the medium and of its thinness, the double-layer capacitor may have a capacitance of 20 to 100 $\mu F/cm^2$ depending on the natures of the metal and the solution. If the electrochemical interface is *polarisable*, that is, impermeable to electric charges, then the interface behaves as a "molecular" non-ideal capacitor (3), that is, because of the usually non-linear response of molecules to an electric field, the charge/potential relationship differs from that of a conventional capacitor (Figure 1). Thus, a mercury/aqueous solution interface, the "classic" polarisable electrode, may have a *differential* capacitance ($dQ/d\Delta V$) of several tens of $\mu F/cm^2$ at some potentials, with corresponding lower *integral* capacitance ($Q/\Delta V$).

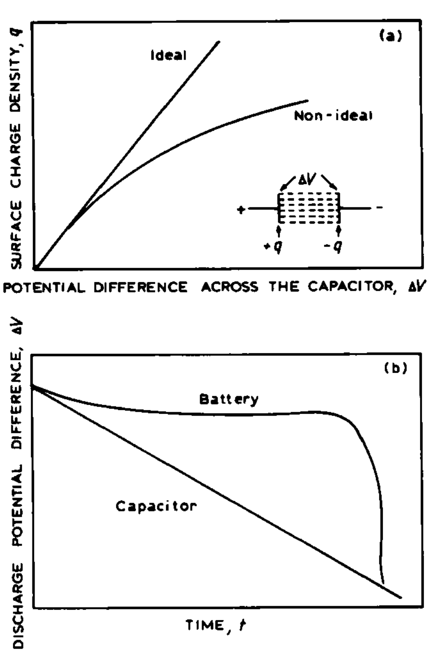


Fig. 1 (a) Charging curves for ideal and non-ideal capacitors. (b) Discharging curves for an ideal capacitor and a battery

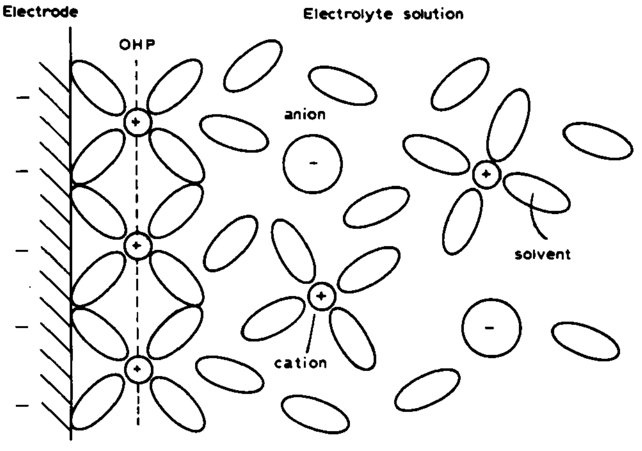


Fig. 2 The electrical double layer at the interface between an electrode and an electrolyte solution. OHP (Outer Helmholtz Plane) is the plane of closest approach of solvated ions to the electrode surface. The OHP acts as one of the plates, on the solution side, of the double layer capacitor

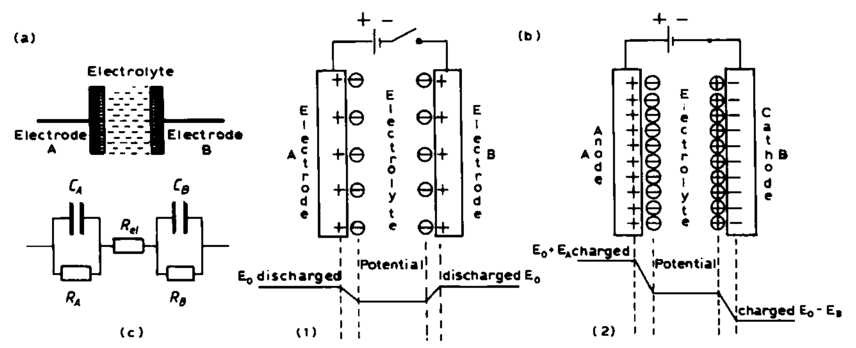


Fig. 3 (a) Cross section through a practical electrochemical double layer capacitor. (b) Profiles of the potential across an electrochemical capacitor in the discharged (1) and charged (2) conditions. (c) Simplified equivalent electric circuit for an electrochemical capacitor. The capacitance and reaction resistance for the two electrodes, and the electrical resistance of the interelectrode gap are shown

The latter is of interest for practical situations.

An electrochemical interface cannot be charged by working with a single electrode. Thus, an electrochemical capacitor has the same features as a battery: two electrodes in contact with an electrolyte, see Figure 3a, but with dramatically reduced size, and with a fundamentally different mechanism of charging and discharging, Figure 3b. In addition, electrochemical capacitors carry no polarity under open-circuit conditions. It is to be noted that for such a system to work properly, interfaces are needed which behave reversibly to either direction of current flow; additionally, the total capacitance is half the value of a single interface, since the two electrodes are two capacitors in series, see Figure 3c.

Mention should be made of another class of condensers – the electrolytic capacitor – which could be confused with electrochemical capacitors since they are also based on an electrochemical mechanism. However, these in fact are conventional capacitors because they consist of two metal plates separated by a thin oxidic dielectric which is *electrolytically* grown on the metals. Aluminium or tantalum oxide is usually used as the dielectric. No spontaneous charge separation takes place at the interfaces – double-layer charge is not involved. Moreover, precautions must be taken with the electrical connections since wrongly connected electrolytic capacitors may explode (due to a breakdown of the dielectric). Furthermore, the relative permittivities of the dielectrics: aluminium oxide (7–10), tantalum oxide (25–27), titanium oxide (48) and other oxides are small, and the thickness of the dielectric is high, compared with their coun-

Properties of Different Electrical Energy Stores

Device	Energy density, Wh/dm^3	Power density, W/dm^3	Cycle life
Batteries	50–250	150	$< 10^4$
Electrochemical capacitors	5	$> 10^5$	$> 10^5$
Conventional capacitors	0.05	$> 10^8$	$> 10^6$

Taken from Ref. 1

terparts in the electrical double layer capacitor.

From the above it is clear that batteries are needed when a supply of electrical energy is required for a long period of time at low current, whereas double-layer capacitors are useful for the rapid supply of large quantities of electricity over a short time. In order to improve the power delivered by these capacitors, the amount of charge stored per square centimetre of geometric surface area should be maximised while the potential window of operation should be enlarged as much as possible.

In practice an ideal double-layer capacitor can hardly be realised, since spurious surface redox reactions usually accompany double-layer charging and this is in fact the case with carbon capacitors, which are the prototype of this category (4). In these carbon capacitors surface oxidic structures (for example quinone groups) are always present (5). "Supercapacitors" are a particular category of electrochemical double-layer capacitors in which *capacitive*, Q_C, and *surface* Faradaic, Q_F, charges coexist. For instance, if a monolayer of atomic hydrogen is formed on a platinum electrode by cathodic discharge:

$$H^+(aq) + e \rightarrow H_{ad}(Pt) \qquad (v)$$

Equation (v) resembles the reaction occurring in a battery, but is confined to the surface of the electrode. The charge associated with hydrogen adsorption is approximately 200 $\mu C/cm^2$ of *real* surface area. This charge, divided by the potential range from which it is transferred, constitutes a *pseudo-capacitance* since it is not associated with a purely capacitive phenomenon (2, 6).

However, $Q_F + Q_C$, the latter being the "true" double-layer charge, dramatically increases the power of an electrochemical capacitor, while affecting the response time very little; hence the term "supercapacitor" which these devices are often called (2). The example described by Equation (5) would not constitute an excellent supercapacitor, since the potential range of effective operation is too narrow, being only about 0.3 to 0.4 V.

In this paper we will focus our attention on the transition metal oxides of the platinum group, particularly ruthenium and iridium, RuO_x and IrO_x. The interesting and promising properties of these oxides will be illustrated for potential applications in supercapacitors.

Background of Supercapacitors

Although the capacitive properties of electrochemical interfaces have been known since 1879 from work by Helmholtz (7), practical applications of the electrical double-layer for energy storage have only recently become of worldwide interest (8).

Grahame's pioneering studies on the electrocapillarity of mercury in 1947 (9) were completed in the early 1960s by investigations carried out on the adsorption of hydrogen on platinum, palladium, rhodium, iridium and gold (10). At that time the Standard Oil Company (SOHIO) was aware of the high value of the double-layer capacitance of carbon electrodes in fuel cells (11), and in the summer of 1962 a 3 cell/6 V carbon capacitor, the size of a large car battery, was able to power a canoe on a lake for about ten minutes. In April 1969 a brochure was prepared for their prospective customers entitled: "Non-polar Electrokinetic Capacitor, 0.6 Farad, 6 Volts". However, the research was terminated in 1971 and the technology was later licensed to Nippon Electric Company, who have been manufacturing "Super Capacitors", since 1979 (12). Almost at the same time, Matsushita designed their "Gold Capacitor" using activated carbons in organic electrolytes (13).

Electrodes based on platinum metals oxides were developed in the 1970s (14); they were designed originally for use as dimensionally stable anodes in chlor-alkali cells (15). Later ruthenium oxide was used in the Pinnacle "Ultracapacitor" (16), while in 1990 Giner Inc. presented their RuO_x/carbon/Nafion capacitor (1, 17).

Future Applications of Electrochemical Capacitors

Electrochemical capacitors seem to open novel dimensions in power engineering and power electronics, offering enormous specific capacitance as their particular advantage. Compact electronic components with very large capacitances could be manufactured. Electrochemical capacitors have potential power densities of over 3 kW/kg and 10 kW/dm³ (1), exceeding the power densities of high-power batteries by a hundredfold. Energy densities of about 5 Wh/dm³ are higher than those of present-day ceramic and electrolytic capacitors. Conventional capacitors can store up to 1 C of charge, while batteries can store 10^4 to 10^8 C, therefore electrochemical capacitors could fill this gap. In contrast to accumulators, electrochemical capacitors can be charged and discharged in shorter times and their rechargeability is almost unlimited. Various applications for electrochemical capacitors have been proposed (8, 18):

- High power devices for energy storage systems, voltage stabilisers, power failure protection, pulsed lasers, satellite antennas, space communication systems, electric vehicle propulsion, starters in motor vehicles, regenerative braking, medical equipment such as defibrillators, electronic fuses in the mining industry and smart weapons.
- Battery substitutes for consumer electronics: memory back-up in computers, displays, video recorders, solar watches and toys.
- Replacing conventional capacitors in electronics for filters for power supplies, controlling equipment and alarm safety devices. Capacitors can protect sensitive electronics against power fluctuations, line transients and shutdowns.

The power system could be a hybrid arrangement with an energy storage capacitor for handling the peak power and a battery for handling the sustained load.

Technical Details

A simple electrochemical plate capacitor is formed from two plane electrodes dipping into an electrolyte. Two double-layer capacitances are thus combined in series and can be charged by applying a voltage. The initial high charging current decays to zero after a few seconds or minutes of charging. The charging voltage should not exceed the decomposition voltage of the electrolyte. Higher nominal voltages from the capacitor can be realised by combining in series several electrodes to form a bipolar stack.

Electrochemical capacitors display some features which are unknown to conventional capacitors, and some which can be compared to those of electrolytic capacitors (5, 19). An ideal double-layer capacitor would have a perfect dielectric with an infinitely large capacitive reactance which would cause a phase shift of 90° between the AC voltage and AC current flowing through. Owing to the internal resistance of electrodes and electrolytes actual electrochemical capacitors show a phase shift of less than 90°. In practice a pseudocapacitance is measured which is strongly dependent on frequency, temperature and voltage. The impedance of capacitors can generally be modelled by an equivalent electric circuit consisting of the isolated resistances and pseudo-capacitances of the electrodes, see Figure 3c, the electrolyte resistance and, if necessary, a series inductance (16, 17).

The ability to store energy increases as more bipolar electrodes are used and larger active electrode areas are chosen. The search for highly capacitive electroactive materials has led, among other materials (5), to ruthenium oxide (20) and iridium oxide (21, 22).

Noble Metal Oxides as Active Materials

The surface of an oxide in the presence of water molecules becomes covered by a carpet of OH groups, that is, it is hydroxylated, see Figure 4 (23). Platinum group metals are known to form oxides in a range of oxidation states from +2 up to +8. Thus, when RuO_x is placed in solution and its potential is altered, for instance made more cathodic (reduction), the valency state of the *surface* metal atoms changes while being compensated by an exchange of protons with the solution (24):

$$RuO_x(OH)_y + \delta e + \delta H^+ \rightarrow RuO_{x-\delta}(OH)_{y+\delta} \quad (vi)$$

Reaction (vi) is reversible for both RuO_x and IrO_x, taking place over a potential range of about 1.4 V in aqueous solution, and limited only by the electrochemical decomposition of water – oxygen is evolved at more positive potentials, and hydrogen is formed at more negative potentials.

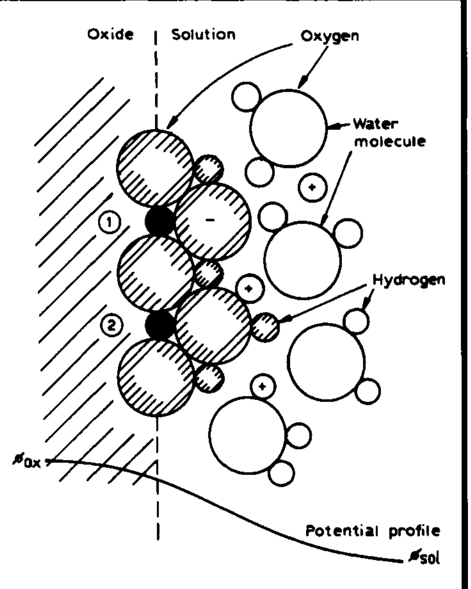


Fig. 4 Structure of the interface between an oxide on a capacitor plate and an electrolyte solution, with the potential profile across the interface. Positively (1) and negatively (2) charged surface sites are shown

The pseudo-capacitive charge exchanged in Reaction (vi) involves all the active metal sites of the oxide surface. On the basis of a structural model, charge Q can be calculated to be about 160 to 200 $\mu C/cm^2$ over a potential range of about 1 V when ruthenium ions are formally oxidised from +2 to +4. The associated capacitance is thus about 0.2 mF/cm^2 of real surface area. However, interest in utilising RuO_x is due to the fact that this oxide, and also IrO_x, can be obtained in a morphological state, which increases its surface area enormously. A layer of a few micrometres thickness can carry a charge of up to 1 to 2 C/cm^2 of geometric surface, which is equivalent to a surface roughness of 500 to 1000. Thus, a RuO_x supercapacitor could provide a capacitance of 0.5 to 1 F/cm^2, which is equivalent to about 25 to 50 F/g of active material.

The above figures are only an example. In fact, the properties of RuO_x depend dramatically on the details of its preparation and on the chemical composition of the active layer which may contain other components. The good response of RuO_x and IrO_x is not only due to their surface and morphological properties but also to their excellent electrical conductivity. This prevents the penetration of electric field into the bulk which would lower the capacitance associated with space charge effects, which can be detrimental with carbon materials (5).

RuO_x and IrO_x can be prepared in various ways and several methods have been described (14). For instance, active electrodes for electrolysis cells can be prepared by the thermal decomposition of suitable precursors (25). The nature of the precursor, the way the precursor is applied to the support, the temperature of calcination, and other parameters, all have a marked effect on the final surface response (24), which requires several complementary experimental approaches for its full evaluation. However, the most straightforward technique for *in situ* characterisation of the surface response is cyclic voltammetry.

In cyclic voltammetry a potential, which changes linearly and periodically with time, is applied to an electrode, while the current response is recorded. The cyclic voltammetric response of an ideal capacitor is illustrated in Figure 5, where the constant capacitance results in charging at constant current while ΔV is linearly increased; v is the potential scan rate:

$$I = Q/\Delta t = C\Delta V/\Delta t = Cv \qquad \text{(vii)}$$

From Equation (vii) it is clear that for a non-ideal capacitor the current response will be

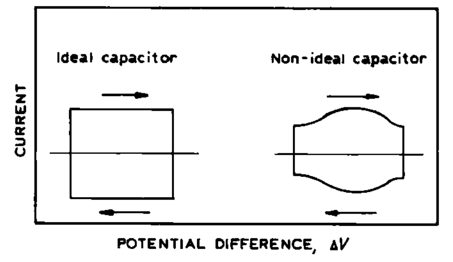


Fig. 5 The response of an ideal and a non-ideal capacitor to cyclic voltammetry. The constant capacitance of an ideal capacitor results in charging at constant current while ΔV is linearly increased, while for a non-ideal capacitor the more the capacitor departs from ideality the more the current response will be non-linear

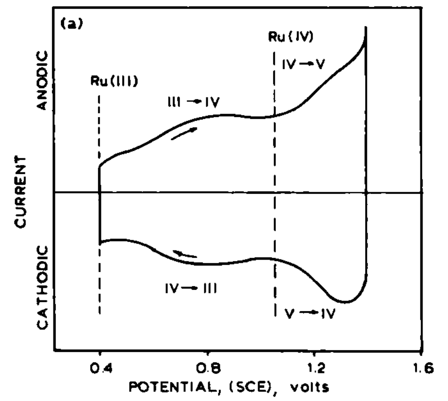
more non-linear the more the capacitor departs from ideal behaviour.

In Figure 6(a) a typical cyclic voltammetric curve for RuO_x is shown (26). It is interesting to see how much the response approaches that of a conventional capacitor despite the dramatically different nature of surface charging. The broad humps are associated with surface redox transitions, as outlined by Equation (vi). The broadness of the peaks can be explained in terms of a large heterogeneity in the surface sites. Figure 6(b) compares the cyclic voltammetric curves of different materials. It is more difficult to distinguish definite redox transitions for IrO_x although the response is still typical of a non-ideal condenser (27). Conversely, the cyclic voltammetric response of a battery-like material or of a homogeneous surface site distribution would result in sharp, high peaks which are unsuitable for use in double-layer capacitors. The response of a NiO_x electrode is shown for comparison.

Ruthenium and iridium oxides can also be prepared by anodic electrolytic growth on the parent metals. A very high charge is also obtained in this case, but the voltammetric response indicates that hydrous oxides with *bulk* oxidation/reduction transitions are obtained in similar circumstances. In this state the electrode resistance, which is deleterious, increases, while the time response becomes slower (27, 28).

Integration of the cyclic voltammetric curves gives the surface charge density (q^*, measured in C/m^2) associated with charging/discharging, which is a primary parameter in the evaluation of oxide electrode properties. Much fundamental work has been devoted to the characterisation of oxide electrodes (24), and a decrease in surface charge density has been found as the calcination temperature is increased. Figure 7 illustrates the case for IrO_x: the maximum indicates the borderline temperature below which decomposition is incomplete (29). The surface charge density has been observed to depend on the solvent in which the precursor is dissolved: thus, organic solvents produce a higher charge for IrO_x, probably because they favour the formation of particles of smaller size (30). In addition, RuO_x prepared from the nitrate exhibits a higher value of surface charge density than when it is prepared from the chloride (31).

The various morphological analyses carried out on these oxides have shown that the layer possesses a compressed powder structure, see Figure 8 (24). In addition to pores being present, crystallites are joined at boundaries which may be permeable to the electrolyte solution. Therefore, the whole layer becomes impreg-



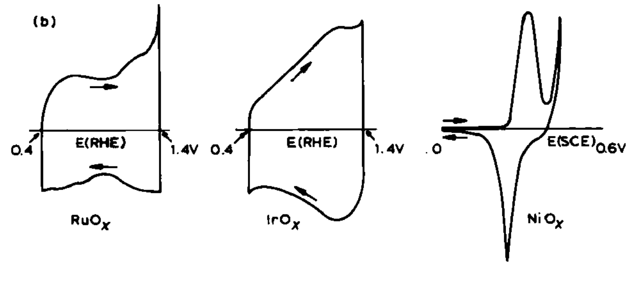


Fig. 6 (a) Typical cyclic voltammetric curve of a RuO_x electrode in acidic solution. Surface redox transitions appear to occur upon potential cycling. (b) Comparison between voltammetric curves for RuO_x, IrO_x, and NiO_x

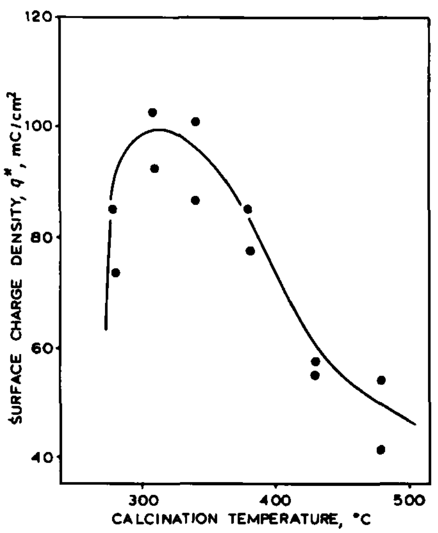


Fig. 7 Variation of the voltammetric (surface) charge density of an IrO$_x$ electrode with the calcination temperature

nated with the electrolyte solution and this results in a very high oxide/solution interface area.

Proton exchange is easy and fast at the outer (macro) interface, but it may be limited by mass transfer and other problems at the inner (micro) interfaces. This can be inferred in a number of ways, from the dependence of the surface charge density on the pH of the solution (surface charge density decreases if measured at intermediate pH), from the exchange rate of tritium in solution, from the in-depth profile of proton concentration, and in particular from the dependence of surface charge density on the rate of application of the electrode potential in cyclic voltammetry (24). Figure 9 shows an example for RuO$_x$.

A model to separate the inner from the outer surface charge has been proposed on a phenomenological basis (32). If the slow process is proton diffusion toward the inner surface, then surface charge density, q^*, is expected to increase with $\sqrt{t}$, as semi-infinite linear diffusion can be assumed. This is strictly the case as steps in potential are applied. In cyclic voltammetry experiments semi-infinite linear diffusion is not in a steady state since the electrode potential is varied continuously. It is however intuitive, since v (measured in V/s) is proportional to $1/\sqrt{t}$, that q^* should vary linearly with $1/\sqrt{v}$. Extrapolation of the plot to $1/\sqrt{v} \rightarrow 0$ provides a value of q^* corresponding to $v = \infty$, that is to completely frozen diffusion. Hence, q_∞^* should correspond to the charge exchanged by outer surface sites only.

The extrapolation of q^* to $v = 0$ is less obvious, but it has been found that a plot of $1/q^*$ versus $\sqrt{v}$ results in a fairly linear dependence over a broad range of v. These plots give q_0^*, that is the charge exchanged under reversible conditions. It is thought that q_0^* refers to the protons exchanged by all the surface active sites. In conclusion, $(q_0^* - q_\infty^*)$ gives the charge exchanged by the inner surface, which provides an estimation of the porosity of the oxide layer.

The importance of porosity in double-layer materials can hardly be over-emphasised. It is obvious that for pulse applications the response

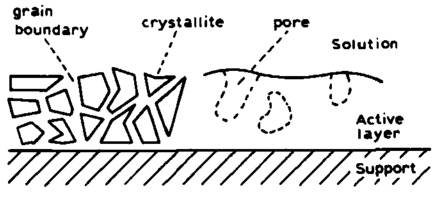


Fig. 8 Morphology of a thick oxide layer, showing crystallites, grain boudaries and pores. The oxide/solution interface area is very large when the layer is impregnated with electrolyte solution

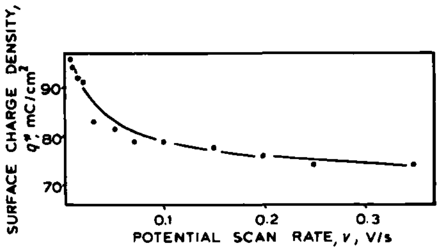


Fig. 9 Variation of the voltammetric (surface) charge of a RuO$_x$ electrode with the potential scan rate

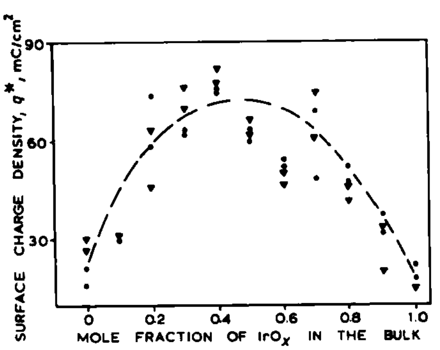


Fig. 10 Dependence of the voltammetric (surface) charge of IrO_x + RuO_x electrodes on composition, represented by the mole fraction of IrO_2 in the electrode bulk; ● in acidic solution; ▼ in alkaline solution

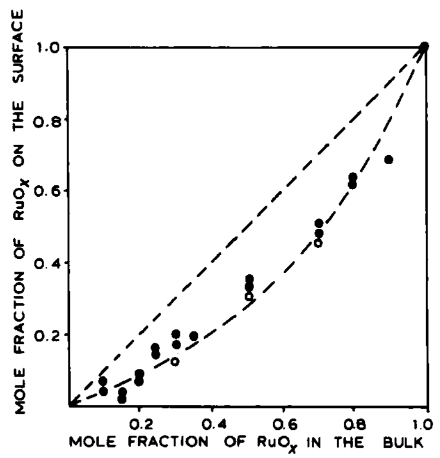


Fig. 11 The surface versus bulk compositions of IrO_x + RuO_x electrodes in mole fractions of RuO_x; ○ is XPS analysis; ● are points at which cyclic voltammetric analysis was performed

of a capacitor may depend dramatically on the nature of the inner surface as well as on the direction of polarisation, since a proton saturated layer may respond faster than a proton unsaturated layer.

Mixed Oxide Layers

Oxide layers used for supercapacitors must have a great ability to store charge, but they must also be resistant to electrolytic media and to charge/discharge cycles. The latter can induce mechanical instability; higher stability can be achieved by combining two or more types of oxides.

As RuO_x is mixed with IrO_x the surface charge turns out to depend on composition, and is usually higher at intermediate compositions, see Figure 10 (33). Moreover, the surface composition differs from the bulk nominal composition, Figure 11 (27). Both q^* and surface composition can be evaluated *in situ* by cyclic voltammetry.

From proton exchange experiments, *inter alia* it is observed that IrO_x is more "hydrous" than RuO_x (24), and therefore, IrO_x can improve AC capacitance at low frequencies. On the other hand, RuO_x displays a very low resistance and can be used to dope insulating metal oxides for application as "diluents" in industrial electrodes. Mechanical "erosion" can also be monitored electrochemically; since q^* is proportional to the oxide loading, erosion is observed to decrease q^* (34). Dissolution of active sites will also decrease q^* since this is accompa-

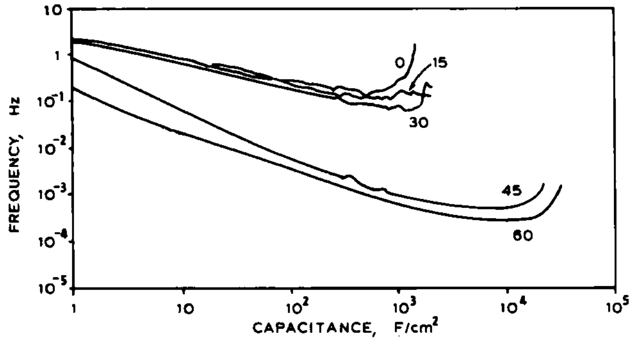


Fig. 12 The effect of the amount of tantalum, measured in mole per cent, on the frequency response of a capacitance of mixed metal oxide single cells

nied by smoothing of the surface (35).

Chemical and mechanical stability in supercapacitors can be improved by mixing noble metal oxides with valve metal oxides, such as titanium oxide and tantalum oxide (36). On the other hand, mixing two or more oxides always results in some deterioration of the high-frequency capacitance since valve metal oxides do not contribute to the electrochemical proton exchange. However, titanium oxide increases the DC resistance, while tantalum oxide may improve the series inductance, see Figure 12.

Conclusions

The oxides of the platinum group metals, particularly RuO_x and IrO_x, possess properties at their interface with aqueous electrolyte solutions which are of great value for their potential use in electrochemical double-layer supercapacitors. The optimisation of their *in situ* response depends on a large number of variables which can be critically controlled only if their surface structure is investigated by a number of complementary electrochemical and non-electrochemical techniques.

The most promising aspects are (a) the very high interfacial capacitance per unit oxide mass due to the specific morphology, which results in a very high surface area, as well as to the specific mechanism of surface charging involving proton exchange with the solution, (b) the fast response to charging/discharging cycles, and (c) the mechanical and chemical stability under repetitive cycles. Finally in order to optimise the response mixing two or more oxides allows the various properties of the oxide layer to be controlled.

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Conducting Polymer Interconnects for Platinum Nodes

Since the development of ultra-small electrical circuitry, molecular electronics and artificial neural networks, the search to find ways of providing electrical connections between such nanosize three-dimensional structures has become a priority. The use of conventional mechanical or photolithographic fabrication techniques is inadequate for direct linking of such structures. Connecting these "molecular wires", by using various chemical techniques to direct the linkage such as conducting organic polymer strands, has been the most successful so far, but a general technique for connecting large numbers of "molecular wires", independently of each other, has not yet been found.

Now, however, researchers at the University of California, San Diego, have demonstrated the ability to interconnect many individual platinum nodes in three dimensions by an electrochemical polymerisation technique (C. L. Curtis, J. E. Ritchie and M. J. Sailor, "Fabrication of Conducting Polymer Interconnects", *Science*, 1993, **262**, 2014–2016).

Their technique is based upon the ability of conductive polymers, such as poly(3-methylthiophene), to be electrochemically switched between electronically conducting and non-conducting states. Pairs of platinum wires in an array, immersed in a solvent of monomer/electrolyte, were independently electrically linked by polymer dendrites on passing an alternating current between them. When an actively polymerising strand electrically contacts a non-conductive strand, the non-conductive strand switches into its conductive state in the region close to the connection. Further polymerisation then occurs in the contacted region to reinforce the connection. The process requires no external mechanical manipulation or lithographic patterning. By using a separate insulating step, sets of electrically independent nodes can be prepared. The insulation of the electrically active links was performed by subsequent electropolymerisation of 4-vinylpyridine or 2-methylthiophene or, more consistently, by dip-coating the connections into a tetrahydrofuran solution of polystyrene.

The polymer connections display several properties relevant to neural networks, fuzzy logic or other nanofabricated model systems. In theory, a large number of nodes could be connected by this method, with the strength of each connection being determined by the conductivity between the node and the network. Therefore, it is expected that with further research, this non-mechanical technique could lead to the construction of complex three-dimensional nanosize interconnected arrays.

High Temperature Palladium Superconductor

Since the first high temperature YBaCuO superconductors were found in 1986, there has been much research to establish their basic mechanism and to find modifying elements which would increase the critical temperature. Copper oxides have usually been employed in these superconductors since they have a very high transition temperature, but no new families of intermetallic compounds with high transition temperatures have been discovered since the niobium binaries in 1953.

Now, however, researchers at AT&T Bell Laboratories in New Jersey, the University of Tokyo and the Technical University, Delft, have reported superconductivity at 23 K in a multiple-phase bulk sample of yttrium palladium boride carbide. (R. J. Cava, H. Takagi, B. Batlogg, H. W. Zandbergen, J. J. Krajewski, W. F. Peck, R. B. van Dover, R. J. Felder, T. Siegrist, K. Mizuhashi, J. O. Lee, H. Eisaki, S. A. Carter and S. Uchida, *Nature*, 1994, **367**, (6459), 146–148).

The transition temperature of this palladium quaternary intermetallic is higher than that of any previously reported for a bulk intermetallic compound. The superconductivity was observed for a narrow range of compositions at relatively low carbon contents. The superconducting volume fraction was large, even though the material was not single-phase. In addition, superconductivity was observed in small quantities in yttrium-palladium-boron alloys with no added carbon. It is suggested that yttrium palladium-boride carbide may be a new family of high-transition temperature superconductors.