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FUEL CELLS AND BATTERIES EMPLOYING POLYACETYLENE
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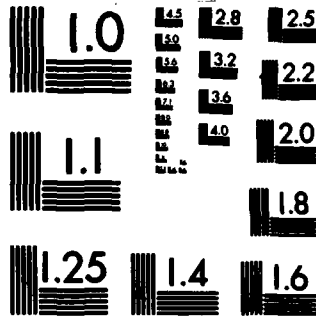
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Fuel Cells and Batteries Employing
Polyacetylene Electrodes in Aqueous Electrolytes

by

A. G. MacDiarmid, R. J. Mammone,
N. L. D. Somasiri and J. R. Krawczyk

Presented at:

11th Energy Technology Conference
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Department of Chemistry
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observations suggest that a large new area, not only of fundamental scientific interest but also of possible potential technological importance, may exist involving the aqueous electrochemistry of $(CH)_x$ and also other conducting polymers.



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FUEL CELLS AND BATTERIES EMPLOYING POLYACETYLENE ELECTRODES

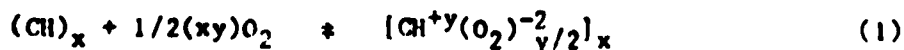
IN AQUEOUS ELECTROLYTES

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Polyacetylene, $(CH)_x$, the prototype conducting polymer, is the simplest possible conjugated organic polymer. It can be prepared in the form of silvery flexible films whose conductivity we have found can be readily increased by ~ 12 orders of magnitude by controlled chemical or electrochemical oxidation, "p-doping", or reduction, "n-doping", to give flexible, lustrous films of "organic metals" conducting in the metallic regime ($\sim < 10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$) (1-3). Until the present studies were performed the practical application of this material had been restricted to uses where oxygen and water could be rigorously excluded since the p-doped material was believed to react with these substances rapidly and irreversibly with complete loss of electrical conductivity. This discussion is limited to a description of the potential use of $(CH)_x$ film as an O_2 "fuel-cell" type electrocatalytic electrode and as a cathode in rechargeable batteries--both systems operating in aqueous electrolytes.

(1) OXYGEN DOPING OF $(CH)_x$ TO THE METALLIC REGIME

We have recently found that trans- $(CH)_x$ can be p-doped (oxidized) to the metallic regime by gaseous oxygen in the presence of an aqueous solution of a non-oxidizing acid such as HBF_4 . This observation is surprising since it is well established that the conductivity of $(CH)_x$ or that of its doped forms is rapidly and irreversibly destroyed on exposure to oxygen and/or air (4,5). It has been reported previously that when cis- $(CH)_x$ or trans- $(CH)_x$ is exposed to oxygen or air for more than approximately one hour irreversible oxidative degradation of the material occurs (4). However, during the first few minutes the conductivity increases by one to two orders of magnitude (from $\sim 10^{-9}$ to $10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ for cis- $(CH)_x$) in a reversible process, viz.,



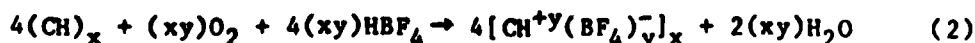
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It is believed the material contains a delocalized polycarbonium ion in combination with an O_2^{2-} or O_2^{-2} ion (4). This system is intrinsically unstable in view of the strongly oxidizing nature of the anion.

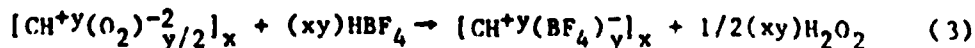
Pieces of trans-(CH)_x (~ 5 x 20 x 0.1mm; ~ 4mg) synthesized as previously described (6), were placed in a 48% (7.4 molar) aqueous solution of HBF₄ in two polyethylene containers. The solutions were previously deaerated by bubbling argon through them for ~ 2 hours. Oxygen was then bubbled continuously through one container so that the samples of film were constantly floating and moving throughout the solution. After a selected time interval one piece of the film was removed and dried in the vacuum system by dynamic pumping and its conductivity (4-probe) was measured. Passage of oxygen was continued for an additional period of time and another sample of film was removed and treated in a similar manner. This process was repeated until all pieces of film had been examined. The solution in the other container was covered with an argon atmosphere and was used as a control. Samples of film were removed at intervals and treated as described above. Some pieces of film from each container were sent for elemental analysis (7) after their conductivity had been measured.

The relationship between the conductivity of the (CH)_x samples and the length of their exposure to their environments is given in Figure 1. The initial conductivity of the trans-(CH)_x was $2.3 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$. The conductivity of the film exposed to oxygen increased by ~ 10^5 during the first day to the beginning of the metallic regime (~ $3 \pm 2 \text{ ohm}^{-1}\text{cm}^{-1}$) and remained constant within experimental error at this value for the following seven days. Experiments are now in progress to determine the stability of the film when exposed to oxygen in aqueous HBF₄ solutions for extended periods of time. The increase in conductivity of the (CH)_x in the control experiment was significantly less, reaching a maximum of only ~ $2 \times 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$. Elemental analysis (Figure 1, footnote 1) of a piece of (CH)_x from the control experiment under argon shows that the HBF₄ used in these studies undergoes negligible reaction with (CH)_x under the experimental conditions employed. The (much smaller) increase in conductivity which does occur is probably related to the presence of minute traces of oxygen remaining in the HBF₄ solution since upon doping, the conductivity of (CH)_x increases very rapidly at first, even at extremely low doping levels.

The overall reaction which occurs can be expressed by the following equation:

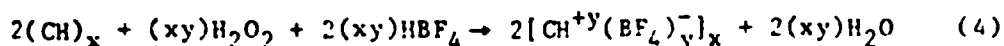


This is consistent with a mechanism involving first the oxidation of (CH)_x to (CH^{+y})_x by the oxygen as given by equation (1) followed by reaction of the $[\text{CH}^{+y}(\text{O}_2)^{-2}_{y/2}]_x$ so formed with the HBF₄, viz.,



We have shown in a separate study that a very dilute solution of H₂O₂ in 48% HBF₄ will oxidize (CH)_x to the metallic regime as given by

equation (4):



A combination of the reactions given by equations (1), (3) and (4) results in the net reaction represented by equation (2).

In the above equations, the anion has been represented, for convenience, as $(\text{BF}_4)^-$. However, it is known that $(\text{BF}_4)^-$ undergoes pH dependent hydrolysis (8) to give species such as $[\text{BF}_3(\text{OH})]^-$, $[\text{BF}_2(\text{OH})_2]^-$, etc. Hence it is not surprising to find that elemental analyses for samples of the oxygen-doped film (Figure 1, footnotes g, h) indicate compositions such as, e.g.

$[\text{CH}^{+0.019}(\text{BF}_3\text{OH})^-]_{0.009}[\text{BF}_2(\text{OH})_2]_{0.010}^-]_x$. The conductivity of $2.9 \text{ ohm}^{-1}\text{cm}^{-1}$ obtained for this 1.9% doped material falls in the same range as that observed for similar levels of doping of *trans*- $(\text{CH})_x$ with iodine ($\sim 0.2 \text{ ohm}^{-1}\text{cm}^{-1}$) (9) and AsF_5 ($\sim 10 \text{ ohm}^{-1}\text{cm}^{-1}$) (10).

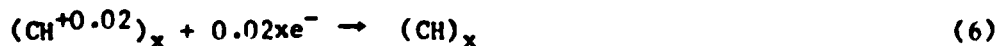
We have recently determined thermodynamic (equilibrium) reduction potentials for polyacetylene in a number of different oxidation states (11). The oxidation of $(\text{CH})_x$ by oxygen or H_2O_2 as given by equations 2 and 4 is consistent with its reduction potentials and those of oxygen and H_2O_2 in acidic media. These studies show that, contrary to previous belief, gaseous oxygen, rather than destroying the conductivity of $(\text{CH})_x$, can be used to dope it to the metallic regime.

(2) USE OF $(\text{CH})_x$ AS AN O_2 -"FUEL CELL" TYPE (ELECTROCATALYTIC) ELECTRODE

The p-doped polyacetylene synthesized as described in the preceding section may be electrochemically reduced, i.e. "un-doped", using an appropriate counter electrode in a spontaneous process with concomitant production of electricity. For example, if a piece of $[\text{CH}^{+0.02}(\text{BF}_4)^-]_{0.02}^-]_x$ film and a strip of lead are placed in a 7.4M aqueous HBF_4 solution nothing happens. The overvoltage for hydrogen evolution at lead is such that lead does not dissolve spontaneously to any significant extent in the HBF_4 employed. If, however, these two electrodes are now connected via an external wire the lead dissolves, liberating electrons:



The electrons flow through the wire and are taken up by the $(\text{CH}^{+0.02})_x$ ion



resulting in the net electrochemical reduction reaction:



which regenerates $(\text{CH})_x$. The lead, which acts as the reducing agent, is converted to $\text{Pb}(\text{BF}_4)_2$.

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The important point to note is that the $(CH)_x$ can be reconvered back to $[CH^{+0.02}(BF_4)^{-0.02}]_x$ in 7.4M aqueous HBF_4 solution, if one wishes, by bubbling oxygen over it while it is immersed in the acid solution as given by equation 2. Hence, if oxygen is constantly bubbled over the polyacetylene electrode it is possible to continuously chemically oxidize the polyacetylene to $[CH^{+0.02}(BF_4)^{-0.02}]_x$ as rapidly as it is reduced electrochemically according to equation 7. Hence, neither the chemical composition nor the total mass of the p-doped polyacetylene electrode changes during the reaction at steady state, i.e., the p-doped polyacetylene acts as a "catalyst electrode" permitting the overall reaction:



to take place. The $(CH)_x$ is therefore acting as a fuel-cell type electrode for oxygen, the oxidizing agent being elemental O_2 , the "fuel" being lead and HBF_4 . It is clear that the operation of the $(CH)_x$ electrode in this system is completely different from that of a conventional battery electrode during either charge or discharge conditions. In a battery the chemical composition and/or the total mass of the electrode changes. It should be noted that although the composition of the actual catalyst in a working cell is $[CH^{+y}(BF_4)^{-y}]_x$, the material that is placed in the cell originally is simply neutral activated $(CH)_x$.

In these preliminary experiments, in which no attempt has been made to optimize conditions for maximum performance, a steady state short circuit current, I_{sc} , of $\sim 0.4 \text{ mA/cm}^2$ of $(CH)_x$ is obtained simply by bubbling O_2 over the surface of the $(CH)_x$ film immersed in the electrolyte. Since the bulk density of the film is $\sim 0.4 \text{ gm/cc}$ and the density of the $\sim 200\text{\AA}$ fibrils comprising the film is $\sim 1.2 \text{ gm/cc}$ the material is therefore approximately two-thirds void space. Experiments are now in progress to force the oxygen through the porous film. Such a modification in design is expected to increase the current to significantly higher levels. This is evidenced by the observation that if oxygen is bubbled over the film for ~ 1 hour when it is not connected to the lead anode so as to permit the interior portions of the film to become oxidized to a somewhat similar level to the outer surface, a short circuit current of $\sim 10 \text{ mA/cm}^2$ is obtained. The open circuit voltage, V_{oc} , of the cell after the 1 hour exposure to O_2 , immediately before the short circuit current measurement was ~ 0.74 volts.

The effect of gaseous oxygen on the current produced by the cell is shown in Figure 2. The film was initially "activated" by electrochemically p-doping it to $[CH^{+y}(BF_4)^{-y}]_x$, ($y \sim 0.06$) in a $CH_2Cl_2/(Bu_4N)^+(BF_4)^-$ electrolyte. A 1.1 cm^2 ($\sim 0.1 \text{ mm}$ thick) piece of $[CH^{+0.06}(BF_4)^{-0.06}]_x$ film was attached to a platinum wire by mechanical pressure and is shown in the inset to Figure 2. The platinum wire attached to the film and the area of the film touching the platinum was covered with molten paraffin wax in order to prevent contact with the electrolyte. It was then reduced, "undoped", by applying a constant potential of 0.01 volts across the cell. The initial current, given in the decreasing left-hand curve in Figure 2, shows

this reduction effect. This activation process is believed to render the film more wettable by the aqueous electrolyte. When the film had been almost completely reduced to $(CH)_x$ the oxygen stream was turned on and off and the current was recorded as given in Figure 2. The film was then severed from the platinum wire by means of a razor blade, by cutting through the wax-covered portion of the film as shown by the dotted line on the electrode configuration given in the inset to Figure 2. When oxygen was bubbled over what then remained of the electrode only a minute increase in current was observed thus proving that the $(CH)_x$ film, not the platinum current collector, was responsible for the observed phenomenon. In another experiment, after turning the oxygen stream off, argon was bubbled through the solution to remove dissolved oxygen. The current fell to an even lower value ($\sim 0.02\text{mA/cm}^2$). Experiments are now in progress to determine the optimum acid strength to be used in the electrolyte in order to obtain maximum currents, voltages and recyclability, etc.

It should be stressed that the potential of the oxygen catalyst electrode is determined by the value of y in the steady-state composition of the $[CH^{+y}(BF_4)^-]_x$ comprising the electrode. The mechanism by which the $(CH)_x$ is converted to $[CH^{+y}(BF_4)^-]_x$, i.e., whether it is by a four-electron reduction of O_2 to $2O^{2-}$ (to produce H_2O) as given by equation (2) or whether it is by two two-electron reduction steps as given by equation (3) (to produce H_2O_2) followed by the reaction given in equation (4) is immaterial. The role of $(CH)_x$ in acting as a catalyst electrode for the net reduction of O_2 is completely different from the catalytic role of a material such as platinum. In the latter case, the potential of the electrode will depend critically on the degree to which four-electron or two-electron reduction steps are involved.

It should also be stressed that lead has been used in this study of the electrocatalytic properties of a $(CH)_x/O_2$ electrode purely as a convenient counter and reference electrode. It should not be implied that lead should be considered as a "fuel" in any practical oxygen fuel cell system! Studies are in progress to investigate other "fuels", particularly organic compounds as a replacement for lead, especially at a $(CH)_x$ electrocatalytic counter electrode.

Although it is as yet far too early to make any realistic predictions, these unexpected catalytic properties of a conducting organic polymer suggest that $(CH)_x$ and possibly other conducting polymers might be useful either in fuel cell-type processes for the generation of electricity using oxygen as an oxidizing agent, or for the facile oxidation of certain organic or inorganic compounds to give useful materials not readily synthesized by other methods.

(3) USE OF POLYACETYLENE AS AN ELECTRODE MATERIAL IN RECHARGEABLE BATTERIES EMPLOYING AQUEOUS ELECTROLYTES

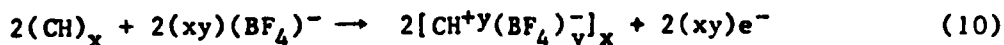
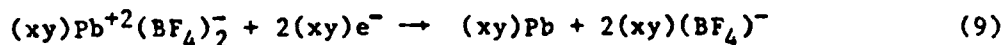
A number of studies during the past four years have demonstrated that polyacetylene and possibly other conducting polymers might serve as good electrode-active materials in rechargeable storage batteries employing non-aqueous electrolytes. Neutral $(CH)_x$, p-doped (oxidized) $(CH)_x$, e.g. $(CH^{+y}A^-)_x$ and n-doped (reduced) $(CH)_x$, e.g. $(M^+CH^-)_x$

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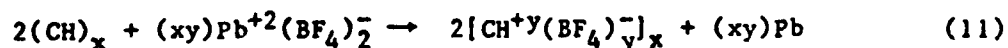
have been employed in various combinations both with themselves or with other anode- or cathode-active materials (2,3). If doped polyacetylene were stable in water it would be preferable to use aqueous electrolytes. Aqueous electrolytes have greater conductivities than non-aqueous electrolytes, hence the power delivered from a battery employing an aqueous electrolyte might be expected, all other things being equal, to be greater than that delivered from a battery employing a non-aqueous electrolyte. Until very recently it has been commonly believed that p-doped polyacetylene is rapidly decomposed by water. However, we have found that this is not necessarily the case, the information given in the preceding two sections showing, for example, its unexpected stability in aqueous acid solution.

We have now found that polyacetylene film may be electrochemically oxidized to $[\text{CH}^+\text{A}^-]_x$ and then subsequently electrochemically reduced in aqueous acid solution. For example, if $(\text{CH})_x$ in a 7.4M solution of HBF_4 containing dissolved $\text{Pb}(\text{BF}_4)_2$ is used in combination with a lead counter electrode, average doping levels of ~ 6% (as measured by the coulombs involved in the oxidation process) can be readily obtained (12).

The charge reactions are:



resulting in the overall charging reaction:



The discharge reactions are the reverse of the above. These battery cells can be charged and discharged in this aqueous electrolyte and show high short circuit currents, promising coulombic efficiencies and good stability on standing in the charged state. For example, a cell containing a ~ 6% oxidized polyacetylene cathode, $[\text{CH}^{+0.06}(\text{BF}_4)_{0.06}^-]_x$, exhibited a V_{oc} of 0.70 volts which changed only slightly (to 0.68 volts) on standing for 7 days. Short circuit currents in the range 100-200mA/cm² were consistently obtained from such cells. These are significantly higher than those observed, (~ 50 mA/cm²) using a 6% oxidized polyacetylene cathode and lithium metal in a propylene carbonate/LiClO₄ electrolyte (13). Coulombic efficiencies of ~ 63% have been obtained in preliminary studies of cells containing ~ 3% oxidized polyacetylene cathodes.

Most surprisingly, we have found that good coulombic efficiencies (~ 90%) using 2.5% oxidized polyacetylene cathodes (lead anode) can be obtained in an almost neutral aqueous electrolyte consisting of a saturated solution of $\text{Pb}(\text{ClO}_4)_2$ (14). This type of cell also shows relatively little decrease in capacity on recycling. Work is in progress to determine what anode materials, including other conducting polymers, might be used in place of lead in conjunction with the polyacetylene cathode in aqueous electrolytes.

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(4) CONCLUSION

These studies show that an organic polymer such as polyacetylene has the capability of acting as an electrocatalytic electrode for the spontaneous reduction of gaseous oxygen at one atmosphere pressure and at room temperature in aqueous acid media. They also show that p-doped polyacetylene can act as an electrode-active cathode material for rechargeable battery cells in certain aqueous electrolytes. These observations suggest that a large new area, not only of fundamental scientific interest but also of possible potential technological importance, may exist involving the aqueous electrochemistry of $(CH)_x$ and also other conducting polymers.

(5) ACKNOWLEDGEMENTS

Preliminary studies of the electrochemistry of $(CH)_x$ in aqueous solution were supported by the University of Pennsylvania Materials Science Laboratory through grant No. DMR-79-23647 from the National Science Foundation. Most of the studies were supported by the Office of Naval Research and by the Defense Advanced Research Projects Agency through a grant monitored by the Office of Naval Research.

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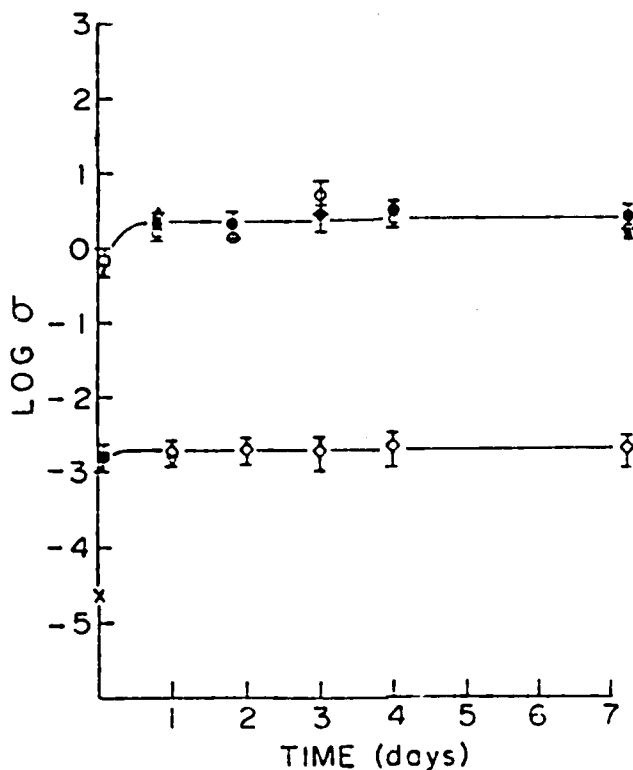


Figure 1: Conductivity (4-probe) of $\text{trans}-(\text{CH})_x$ film as a function of time when immersed in 48% (7.4 molar) aqueous HBF_4 and exposed either to oxygen or argon: (a) \square One sample treated for 2 hours (dried for 2 hours); (b) \blacksquare One sample treated for 2 hours under argon (dried for 2 hours); (c) \bullet Five samples treated for varying lengths of time in the same container (dried for 2 hours); (d) \circ Five samples treated for varying lengths of time in the same container but HBF_4 replaced by a fresh HBF_4 solution every 48 hours (dried for 2 hours); (e) \diamond Five samples treated for varying lengths of time under argon in the same container (dried for 2 hours); (f) \times Conductivity of $\text{trans}-(\text{CH})_x$, ($2.3 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$); (g) \triangle One sample (2cm x 3cm) treated for 24 hours (dried for 24 hours); (h) \blacktriangle One sample (2cm x 3 cm) treated for 7 days (dried for 24 hours); (i) ∇ One sample (2 cm x 3 cm, 18.1mg) treated for 24 hours under argon (dried for 24 hours, 18.5 mg).

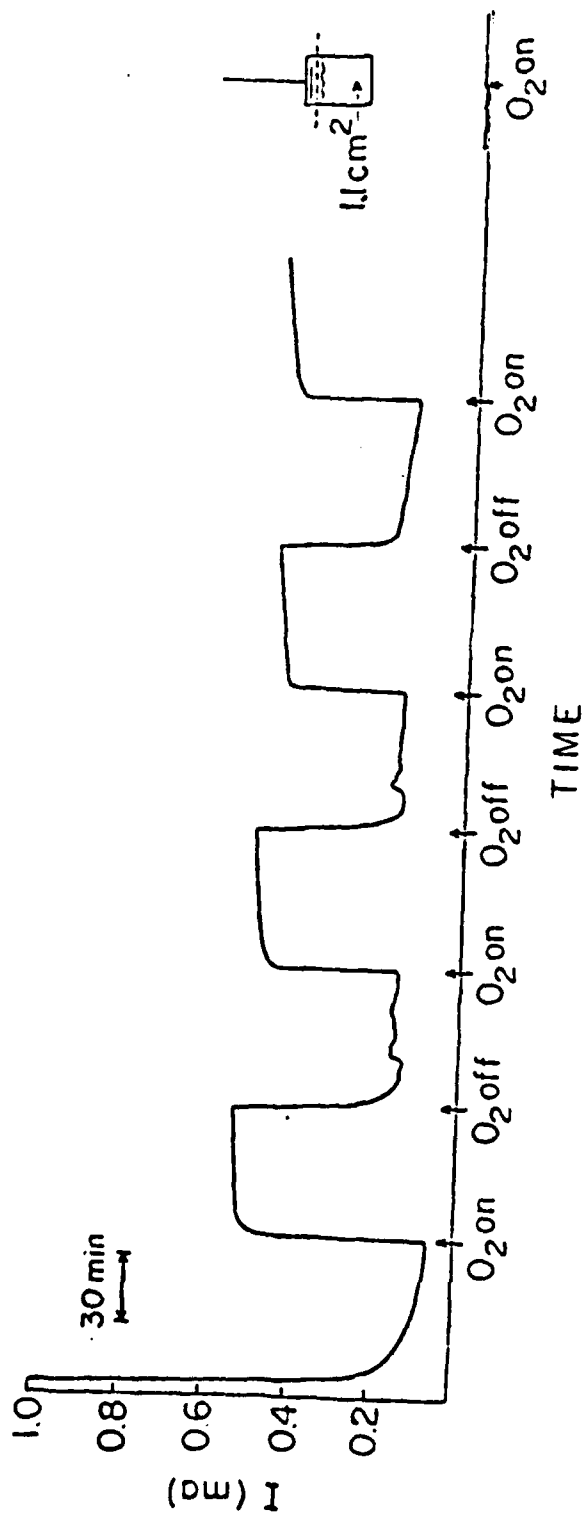


Figure 2: Change in current produced by a (CH)_x/O₂/HBF₄(aq)/Pb cell when an oxygen stream bubbling over the (CH)_x electrode is turned on and off.

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