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Behavior of the Carbon Electrode In Molten Carbonates

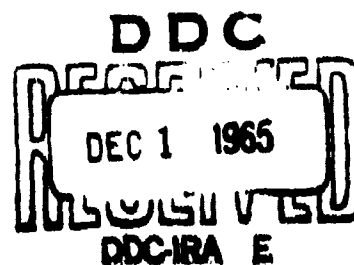
by

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Behavior of the Carbon Electrode In Molten Carbonates

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ABSTRACT

The reversibility of various carbons as electrodes in the ternary carbonate eutectic has been compared. The rest-potential of electrodeposited carbon (-2.2V versus the Danner-Rey electrode) depends on the presence of occluded oxide. The simulation and use of this carbon in a high temperature fuel cell is discussed.

INTRODUCTION

Numerous attempts have been made to design a successful carbon fuel cell, the most notable being the high temperature cells constructed by Baur and others^{1,2,3}. Frequently, fused carbonates or solid electrolytes impregnated with carbonate have been utilized; however, a study of the reversibility of the carbon electrode in such electrolytes appears to be lacking. A recent study⁴ of the cathodic deposition of carbon in molten carbonates suggests that an interesting new approach to the carbon fuel cell.

EXPERIMENTAL

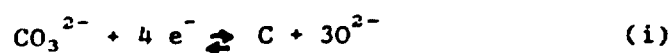
Carbon electrodes were supplied by Pure Carbon Inc. according to the following specifications: (i) Graphitized carbon; density = 1.75 g.cm^{-3} ; porosity = 10%; (ii) 'Active charcoal; density = 0.9 g.cm^{-3} ; porosity = 45%. Electrolytic-carbon electrodes were prepared by the cathodic deposition of carbon onto gold electrodes⁴. The current-voltage curves for the various carbons were obtained in the ternary eutectic of the alkali metal carbonates (Li_2CO_3 , Na_2CO_3 , K_2CO_3 ; mole ratio 43.5: 31.5: 25.0; m. p. 397°C) at 600°C using a potentiodynamic technique described elsewhere⁴.

Fig. (1) shows the polarization curves for graphitized carbon and electrolytic carbon electrodes of the same geometry (1 cm immersion, surface area = 1.0 cm^2), all potentials being referred to a Danner-Rey electrode. The significant feature is the displacement of the rest potential of the electrolytic carbon compared with graphite from -1.3V to -2.2V . This marked enhancement in reducing properties has been shown⁴ to be due to the occlusion of oxide. Further comparison of the current-voltage curves reveals that the electrolytic carbon behaves much more reversibly than the graphitized carbon.

The properties of electrolytic carbon have been simulated by "doping" the active charcoal, in fused sodium hydroxide for 12 hours before transfer to the carbonate electrolyte for evaluation. The polarization curves of the "doped" and "undoped" carbon electrodes (1 cm² immersion) appear in Fig. (2). The undoped carbon has an initial rest potential of -1.45V, but considerable hysteresis appears in the curve due to the inclusion of oxide ions in the electrode on cathodic polarization and their subsequent removal on anodic polarization. The doped carbon has a rest potential of -2.0V and is highly reversible, giving an anodic current density of 100 mA/sq cm at -1.85V. The effectiveness of the doping procedure is best measured by performance of the electrode while passing a continued anodic current. Fig. (3) shows the variation of potential with time at a constant anodic current of 96.5 mA. The potential is seen to rise continuously from the initial value of -1.9V and reaches a value of -0.85V after the passage of 1×10^{-3} F. After this the potential remains constant and the behavior is clearly that of an undoped carbon electrode. From the free volume of the immersed portion of the carbon electrode it is calculated that the amount of NaOH which could be retained is equivalent to 1.1×10^{-3} Eqt. of Na₂O, and the observed doping is seen to be in very good agreement with this.

DISCUSSION

It has been shown elsewhere⁴ that the reversible deposition of carbon corresponds to the reaction,

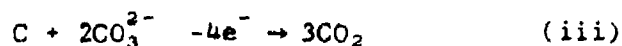


and that the rest potentials of carbon is in accord with the equation:

$$E = E^{\circ} + \frac{RT}{2F} pO^{2-} \quad (ii)$$

$$\text{where } pO^{2-} = -\log_{10} (O^{2-})$$

The different rest potential of the various carbons (e.g. -2.2V for electrolytic carbon and -1.3V for graphitized carbon) are thus explained in terms of changes in the oxide activity at the electrode surface. Electrolytic carbon always contains substantial amounts of occluded oxide, and the establishment of equilibrium (i) is evidenced by the observed reversibility of the electrode towards polarization tests. Under an Ar atmosphere the steady-state O^{2-} activity in the ternary eutectic is low⁷ (ca. 10^{-4} Molar), hence under these "acid" conditions the stoichiometry of the anodic oxidation of carbon is more correctly written as,



The anodic process occurs at a much higher potential than the cathodic deposition reaction and this is seen to be the underlying reason for the irreversibility of the ordinary carbon electrode in molten carbonates.

The behavior of the hydroxide-doped electrode is more complex. It is probable that OH^- ions, on contact with the carbonate, lose water to form O^{2-} ions as has been claimed⁵. The difference in the reversible behavior from that of the electrolytic carbon suggests that this evolved water is influencing the electrode processes in some way, most probably interaction with the carbon to evolve hydrogen⁶:



The enhanced reversibility of the electrolytic and oxide-doped carbons suggests their use as fuel anodes in a high temperature fuel cell. Recently, Busson, Palous, Buvet and Millet⁷ have reported the potential of the reversible oxygen electrode in the ternary eutectic at 600°C ($\text{CO}_2 = 1$ atmos; $\text{O}_2 = 1$ atmos) is -0.53V against the Danner-Rey electrode. By transposing the observed carbon potentials onto the "oxygen scale" the electromotive forces of the following cells may be calculated:

- | | | | | |
|-----|---|---|--|--------------|
| (A) | $\begin{array}{c} \text{C} \\ \text{(active charcoal)} \end{array}$ | $\left \begin{array}{c} \text{ternary eutectic} \end{array} \right $ | $\begin{array}{c} \text{CO}_2 \quad , \quad \text{O}_2 \\ \text{(1 atmos.)} \quad \text{(1 atmos.)} \end{array}$ | EMF = 0.92V |
| (B) | $\begin{array}{c} \text{C} \\ \text{(electrolytic)} \end{array}$ | $\left \begin{array}{c} \text{ternary eutectic} \end{array} \right $ | $\begin{array}{c} \text{CO}_2 \quad , \quad \text{O}_2 \\ \text{(1 atmos.)} \quad \text{(1 atmos.)} \end{array}$ | EMF = -1.67V |
| (C) | $\begin{array}{c} \text{C} \\ \text{(hydroxide, "doped")}\end{array}$ | $\left \begin{array}{c} \text{ternary eutectic} \end{array} \right $ | $\begin{array}{c} \text{C} \quad , \quad \text{O}_2 \\ \text{(1 atmos.)} \quad \text{(1 atmos.)} \end{array}$ | EMF = -1.47V |

Further inspection of the current-voltage curve for the undoped active charcoal electrode reveals that at an apparent anodic current density of 100 mA cm^{-2} the potential rises to -0.93V; that would give a maximum fuel cell voltage, assuming no other energy losses, of 0.4V. It is apparent that cells of type (A) would be rendered quite ineffectual by anodic polarization phenomena; cells (B) and (C) with their larger EMF are more attractive. Fig. (3) can be used to evaluate the hydroxide-doped carbon as a possible fuel electrode. After the passage of $1 \times 10^{-3} \text{ F}$ the carbon is completely "dedoped", and this corresponds to the consumption of approximately 5% of the immersed carbon. This would clearly be unsatisfactory for a practical fuel electrode and a more fundamental approach is required.

It is convenient to define an "ideal fuel electrode" where all the carbon can be consumed under alkaline conditions. Two requirements must be met by this fuel. Firstly, it must have a stoichiometry given either by $(C, 3M_2O)_n$ or by $(C, 6MOH)_n$. Secondly, the carbonate generated at the anode should have the same composition as the main electrolyte. These requirements could be met, in large part, by flowing the appropriate mixture of alkali hydroxides into the carbon electrode while oxidation is proceeding.

ACKNOWLEDGMENTS

The authors acknowledge, with thanks, the experimental contributions and discussions of Bill Baron in various aspects of this work.

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Figure Captions

Figure 1 "Polarization Behavior of Carbon Electrodes"

I Graphitized Carbon

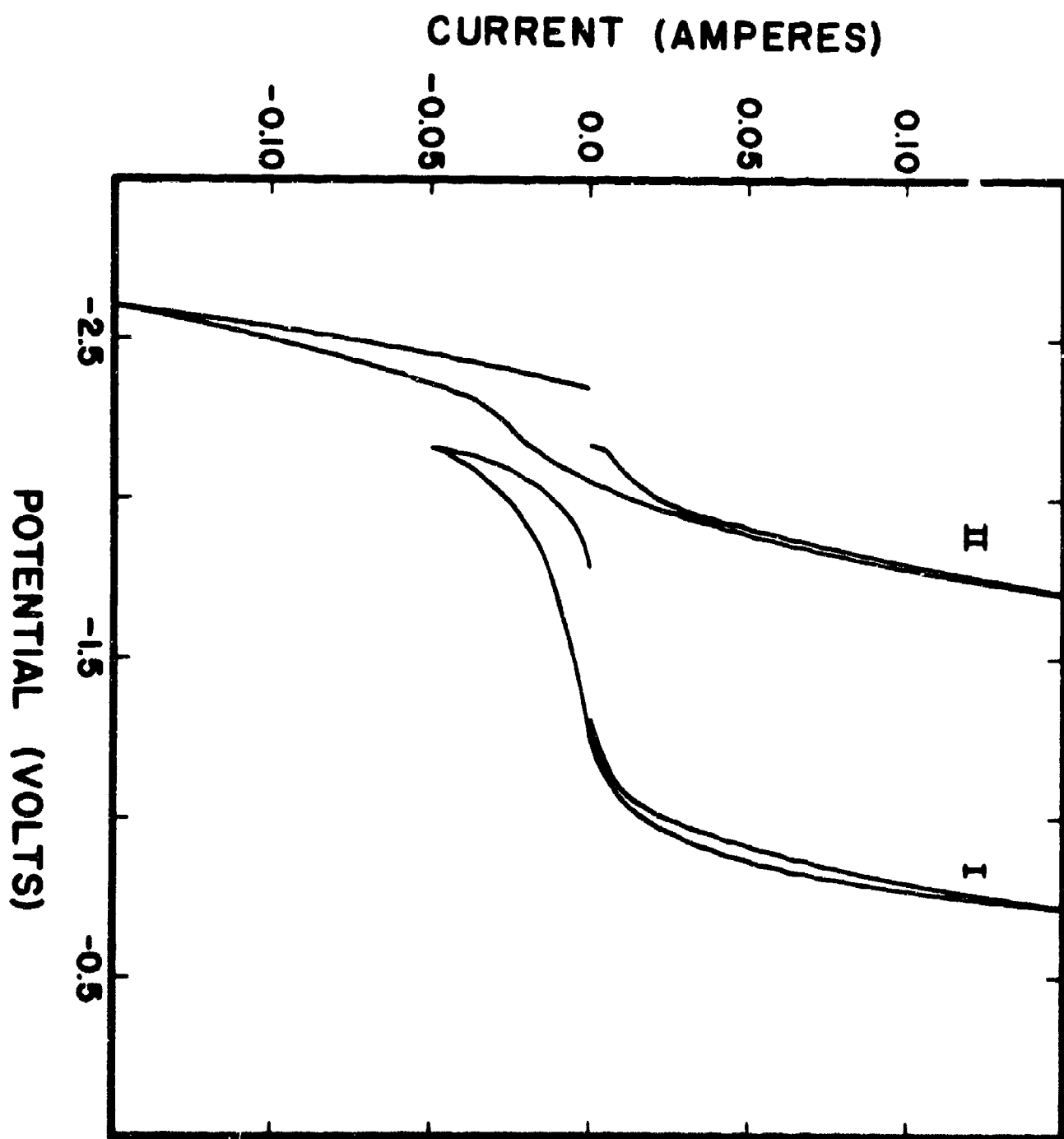
II Electrodeposited Carbon

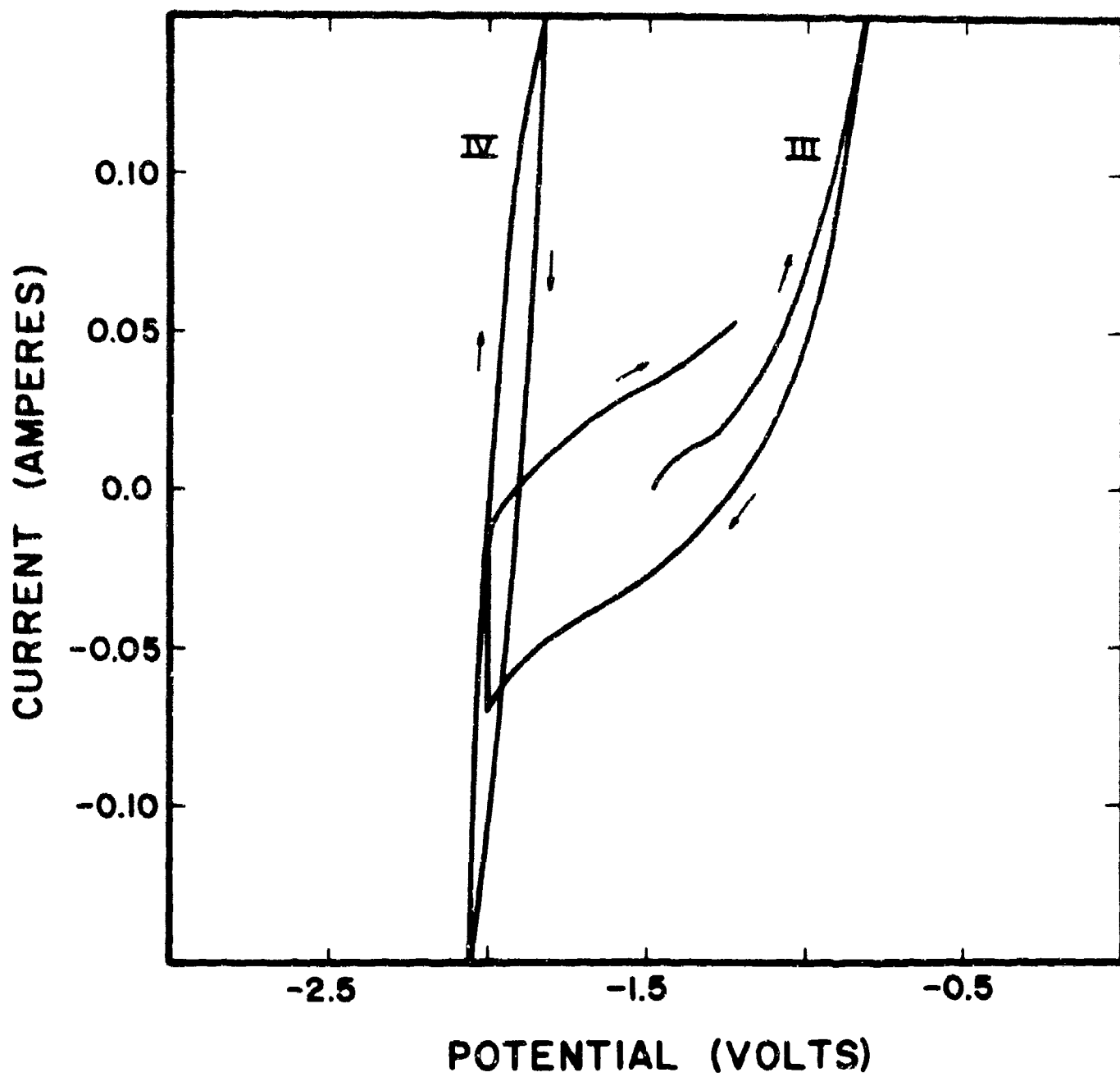
Figure 2 "Effect of Treatment with NaOH in Polarization
Behavior of Carbon Electrode"

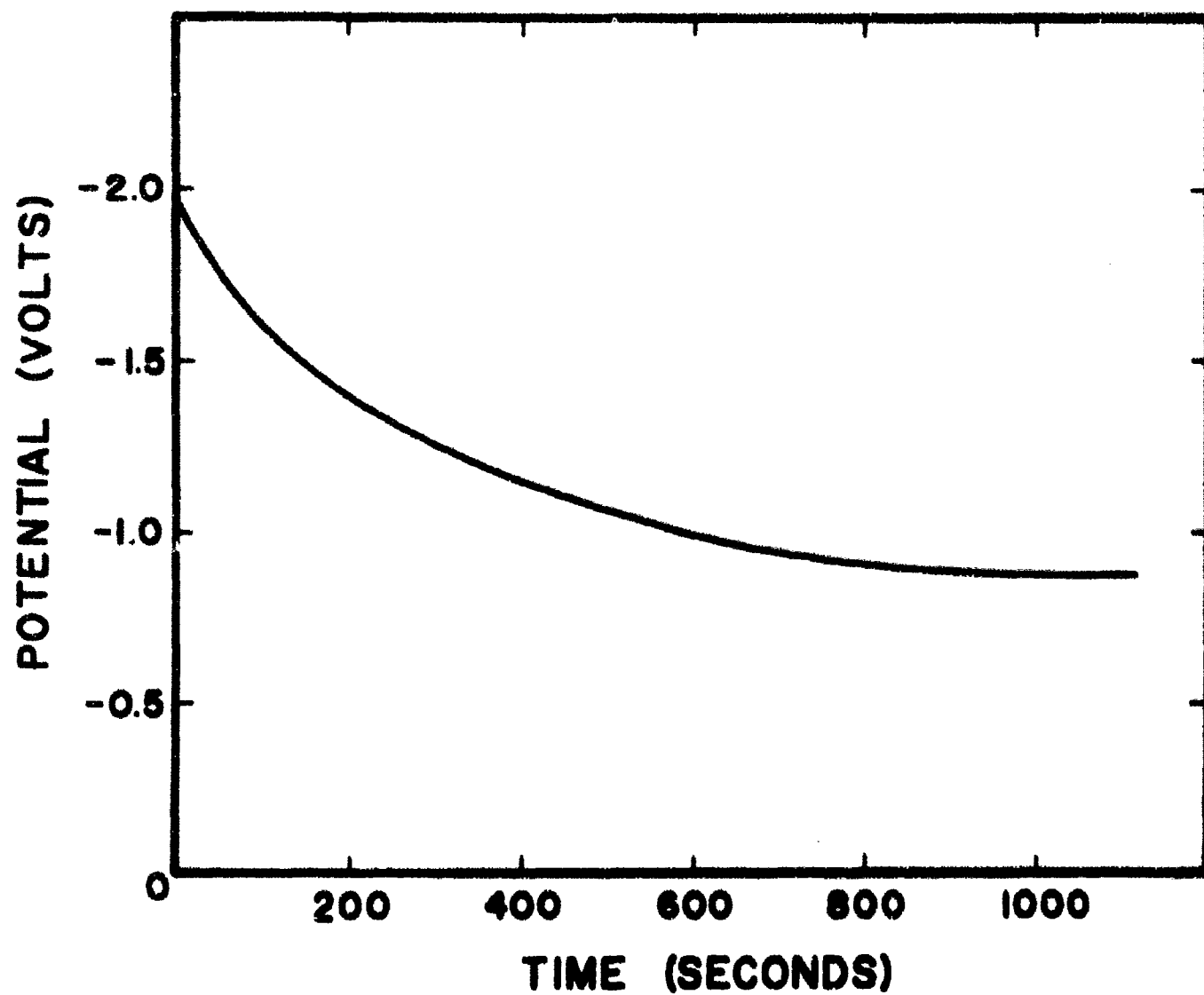
III Active (undoped)

IV Active (doped with NaOH).

Figure 3 "Performance of "Doped" Carbon Electrode:
Potential versus Time Behavior for Constant
Anodic Current of 96 mA cm^{-2} .







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