



PROPOSAL for RESEARCH and DEVELOPMENT

Electrochemical Photosynthesis Process of Oxygenate Compounds

The attempt to find an economic viable solution to the problem of reduction of Greenhouse Gas, in particular, of the carbon dioxide (CO₂), has accumulated in recent years, a large number of research efforts and financial investments.

Examples of multiple approaches to address this important and yet complex energy solution for reduction of Greenhouse Gas, are:

- *Catalytic synthesis obtained with exothermic reactors with the use of hydrogen*
- *Electrochemical proposed solutions*

In the field of electrochemical analysis, PERT has demonstrated in these last years (since 2004) that the use of Fuel Cell with commercial and proprietary membranes can profitably generate oxygenate compounds (*see below the report on the first experiment*).

PERT has continued the studies and has obtained significant results with the use of membranes endowed -through proprietary ideas, using nanotechnology process- of pronounced photovoltaic quality. This innovative application permits utilization entirely and directly for the solar energy to accomplish the process of electrochemical reduction on the CO₂. The process, as the chlorophyll natural synthesis cycle, utilizes the CO₂ and accumulates energy in the form of fuel (ethanol, methanol) releasing O₂ in the atmosphere.

PERT is interested in now expanding our advisory and investor network for maximum development, outreach, and performance. We hope to hear from you and provide additional information.

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April 2007



PROPOSTA per FINANZIAMENTO di RICERCA

Processo di Fotosintesi elettrochimica di composti ossigenati.

Il tentativo di giungere ad una soluzione economicamente valida per la riduzione dei gas serra ed in particolare dell'anidride carbonica ha accumulato in questi recenti anni una notevole quantità di ore di ricerca e di forti impegni economici.

Vari sono gli approcci al problema. Tra questi ricordiamo

- *la sintesi catalitica ottenuta in reattori esotermici, con uso di idrogeno e*
- *la strada elettrochimica.*

Su questa ultima la PERT ha realizzato negli scorsi anni (2004) ricerca con l'uso di **fuel cell** (celle a combustibili) dotati di particolari membrane, ottenendo composti ossigenati (*vedere di seguito il rapporto sul primo esperimento*).

PERT ha continuato lo studio ed ha ottenuto risultati teorici interessanti con l'uso di proprie membrane dotate di capacità di semiconduzione ed effetto foto-voltaico. Cio' permette di utilizzare interamente e direttamente l'energia solare, la quale agisce elettrochimicamente in riduzione sul CO₂. Il processo permette di utilizzare il CO₂ ed immagazzinare l'energia solare sotto forma di combustibile (etanolo, metanolo), al pari della fotosintesi clorofilliana.

Per dare seguito alla ricerca occorrono capitali che la PERT si augura di trovare presso Investitori privati che vogliano dedicarsi ed ottenere la realizzazione di prototipo e lo sfruttamento in produzione di etanolo e metanolo.

Per informazione rivolgersi a:

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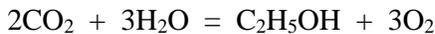
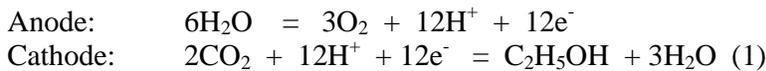
Dec. 19th, 2004

Direct synthesis of light oxygenate fuels (alcohols) from CO₂ and H₂O by a Three Phase Catalytic Reverse Fuel Cell reactor based on Nafion membrane: Preliminary Results

Pert Development Group – Pescara, Italy - Università ‘G. D’Annunzio’ Chieti-Pescara- Italy

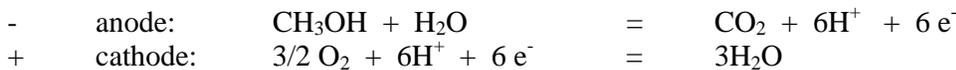
INTRODUCTION

We have experimentally explored the possibility to realize the following reactions:



aimed to the electrochemical production of oxygenate fuels starting from CO₂ and H₂O in a Reverse Fuel Cell apparatus (electrolyser).

Direct Methanol Polymeric Electrolyte Fuel Cells (DM-PEM-FC) based on Nafion protonic membrane can efficiently electrochemically oxidise methanol to CO₂ and H₂O by producing electricity. These fuel cells use Pt and Pt/Ru alloys as anodic and cathodic catalysts, respectively. The two electrodic semi-reactions are:



and the overall reaction is:



Nafion-based electrolytic membrane is highly permeable to protons that, during the cell functioning, move from the anodic to the cathodic side. The membrane, at the same time, completely screens the electrons that, consequently, are forced to move through the external circuitry, from the anode to the cathode, to produce useful work.

It has been demonstrated that PEM-FC, with an appropriate and more efficient anodic catalyst, can electrochemically oxidise ethanol instead of methanol according to the following semi-reaction:





An interesting possibility is to realise the reaction (1) in the backward direction in a PEM-FC operating in reverse mode (electrolyser). In this case CO_2 , H^+ and electrons are fed to the negative electrode (which now is the cathode) to force the reaction (1):



In effect, by this reaction, CO_2 is sequestrated and converted in an useful fuel. A device accomplishing this process could be environmentally interesting, especially if coupled to carbon burning power plants that produce great quantity of CO_2 . In this case, a fraction of the electricity produced could be utilised for the CO_2 reduction.

EXPERIMENTAL

Electrochemical measurements

To preliminarily verify experimentally the feasibility of oxygenate fuels electrochemical synthesis by direct CO_2 reduction we have effectuated different tests on different electrodes utilizing a laboratory scale three electrode cell. The apparatus utilised was a water-jacketed thermostatic glass cell equipped with working, counter and reference electrodes.

The counter electrode was made by a Pt foil having 10 cm^2 surface area. The reference electrode was a Standard Calomel Electrode (SCE) external to the cell itself, but electrically in contact with the electrolyte solution by means of a Luggin capillary placed in close proximity of the working electrode. Two different kind of working electrodes have been utilized, namely: (i) a Pt/C microelectrode used mainly in cyclic voltammetry (CV) scans run to locate the CO_2 reduction potentials; (ii) a Teflon-bonded, porous, Vulcan-XC72 Carbon gas diffusive disk electrode loaded with 5 mg/cm^2 Pt:Ru alloy (1:1) and having a surface area of 1 cm^2 .

The working electrode holder was specifically designed in order to expose one side of the disk to the electrolyte solution while the other side was fed with gaseous CO_2 produced by an external CO_2 generator.

H_2SO_4 0.5 M and 0.1 M water solutions were utilised as electrolyte and as source of protons.

Due to their porosity the electrodes were permeable to CO_2 which could bubble in solution. This configuration was conceived to help to realize an optimum triple contact with the catalyst particles of the three species, CO_2 , proton and electrons, necessary for the electrochemical reaction. Moreover, this geometry permitted two different kind of experiments, namely: (i) static experiments, where the electrolyte solution was saturated with CO_2 and the cell maintained with a slight CO_2 overpressure; (ii) dynamic experiments, where the CO_2 gas was continuously bubbled through the electrode into the solution and discharged at atmospheric pressure.

Analytical measurements



During the electrochemical tests the electrolyte solution was periodically monitored for the reaction products by collecting samples with a micropipette. The liquid samples were analysed with a gas-chromatograph (GC) equipped with a mass-spectrometer (MS) detector.

RESULTS

All the experiments have been carried out at room temperature. At the beginning, many exploratory tests have been conducted by changing different parameters as the CV scanning rate, the electrode potential, the gas flow rate and the concentration of the electrolyte solution. After this preliminary phase a series of finalised electrochemical tests have been performed and analysed.

Table-1 reports the conditions utilised for the CV measurements. The samples for GC analysis were taken on the fresh solution before any CV run (sample M10), after the second CV run (sample M11) and at the end of the CV series (sample M12). At this point the solution was completely renewed and a series of potentiostatic steps were applied to the working electrode as depicted in Table-2. The steps consisted in a potentiostatic hold (electrolysis) for different times (typically 5 and 25 minutes) at progressively more reducing potentials from 0.6 V vs SCE down to 0.1 V vs SCE. The samples M13 to M 22 were taken at the potentials and times indicated in Table-2 and GC-MS analysed.

The final series of runs consisted in potentiostatic holds (electrolysis) for different times, in a fresh H₂SO₄ 0.1 M electrolyte solution, with the potential fixed at 0.2 V vs SCE, as depicted in Table 3.

DISCUSSION

Table 5 reports the main products detected by GC-MS from the different samples. It is interesting to note that the most interesting products, those having a structure close to alcohols (Table 5: 1,4-butandiol and cyclic pentanol) are formed at potential close to 0.6 V vs SCE. This latter potential is the oxidation potential of the methanol to CO₂ and we may suppose that at this potential the reaction is at equilibrium. By further lowering the potentials the reaction is displaced toward more reduced compounds formed via complex radical reactions.

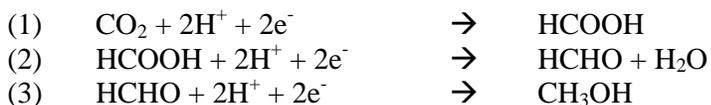
From a preliminary qualitative analysis of the experimental results we can outline the following conclusions:

- 1) Both the Pt/C microelectrode and the Teflon-bonded C/Pt/Ru porous electrodes catalyse the reduction of CO₂ and of the products which form from this reduction;
- 2) If the cell is sealed and the CO₂ is under pressure in static condition, there is formation of many different heterogeneous highly reduced products. These compounds are probably formed by consecutive electrodic reactions favoured by the low diffusion rate, from the electrode surface into the electrolytic solution, of CO₂ reduction intermediates;



- 3) In these conditions the main products detected are alcohols having at least 8 carbon atoms, aldeids with more that 10 carbon atoms and aromatic substituted phenols like toluene (Table 4);
- 4) At longer reduction times there is an increase of H content and a decreases of O content in the compounds detected. This is consistent with reduction reactions that reach final, completely hydrogenated products like toluene;
- 5) The CV traces (Figs 1-4 and Fig 8) show that the oxidation peaks are more pronounced than the corresponding reduction peaks. This can be explained considering both the diffusivity of the formed species which diffuse from the reaction sites (catalyst particles) into the solution and the probable fast recombination of the highly reactive radical intermediate products;
- 6) When the CO₂ gas can flow through the cell and this latter is not sealed the reduction reaction is more efficient (the CV peaks are more marked and reproducible, Fig.4), but the GC-MS analysis shows a lower number of the different species formed (Table 5);
- 7) With the cell not sealed and the CO₂ flowing at atmospheric pressure, for decreasing values of the potential, Figs. 5-7, (increasing electrodic reducing power), we observe (Table 5) mainly the following products (in the order from higher to lower potentials): cyclopentanol, 1,4-butandiol, decanal, substituted phenols, 2-ethyl-1 exanol, while the toluene is not formed. It can be said that in these conditions the reaction can be more easily controlled by varying operating parameters such as potential and time;
- 8) The most interesting products, those having the structure closer to the ethanol (1,4-butandiol; Table 5), are formed at 0.6 V vs SCE. At this potential, which is the re-oxidation potential of methanol and ethanol to CO₂, there is a thermodynamic equilibrium between the reduced and oxidised species. When the potential is furthermore lowered more hydrogenated species are produced, probably via radical formation.

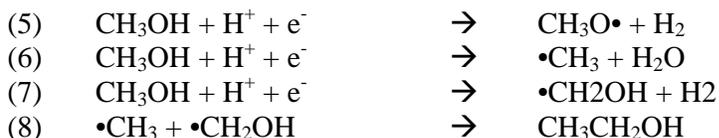
It is worth to note that if we consider the product 1,4-butandiol, which is the lighter product obtained and has the structure closer to that of the ethanol, we can formulate the following relatively simple hypothesis on a radical reaction mechanism for its formation:



This is the well known CO₂ reduction mechanism that can be summarized as:



At this point, intermediate reactions that involve a single proton and a single electron with the formation of radicals that promote different reactions in solution may play a role:

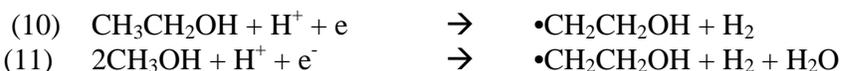




The reaction (5), by the elimination of another H atom and formation of a double bond C=O, can originate a series of reactions which can lead to the formation of aldehydes, while the reactions (7) and (8) can be summarized as:



The compound 1,4-butandiol can be easily formed from the ethanol and methanol by:



Clearly the reaction (11) is less probable, as it comports the presence at the same time of two molecules of ethanol and one of H^+ in contact with the surface of the catalyst, but it can be seen as composed by the consecutive reactions (9) and (10) and, consequently, as the sum of the consecutive steps (7) + (8) + (10).

At this point, the compound 1,4-butandiol can be formed by simply recombination of two radicals:



CONCLUSIONS

We have experimentally demonstrated that CO_2 can be directly electrochemically reduced to 1,4-butandiol on the commercial Pt/Ru catalyst commonly used for methanol fuel cell. The formation of the compound 1,4-butandiol implies the preceding formation, by radical reactions, of both ethanol and methanol. This means that the electrochemical reduction of CO_2 might be optimized to increase the yield of these lighter alcohols by a proper choice of the experimental conditions. To reach this goal many different and important parameters, such as the catalyst formulation, the temperature, the cathodic potential, the time of electrolysis, the cell pressure and the gas flux, etc., can be varied and optimized.



TABLE 1
ELECTROCHEMICAL TESTS

3 CV at different scan rate:

1cv.bin 50 mV/s
11cv.bin 20 mV/s
12cv.bin 5 mV/s

20 CV at 5 mV/s:

13cv.bin 5 mV/s

1 CV at 500 μ V/s:

1meth_check.bin 500 μ V/s

TAKEN SAMPLES

M10 Pristine solution (baseline)

M11 after CVs at 50 and 20 mV/s

M12 after CVs at 5 mV/s and 500 μ V/s

TABLE 2 (H₂SO₄ 0.1M renewed solution)
ELECTROCHEMICAL TESTS

Potentiostatic steps at constant potentials while the cell current was recorderd. An increase of electrode reducing power corresponds to lower potentials.

2expIT600.bin 0.6 V

2expIT450.bin 0.45 V

2expIT300.bin 0.3 V

2expIT200.bin 0.2 V

2expIT100.bin 0.1 V

Final CV:

2CVfin.bin

TAKEN SAMPLES

M13 after electrolysis of 10min at 0.6 V

M14 after electrolysis of 25min at 0.6 V

M15 after electrolysis of 5min at 0.45 V

M16 after electrolysis of 25min at 0.45 V

M17 after electrolysis of 5min at 0.3 V

M18 after electrolysis of 25min at 0.3 V

M19 after electrolysis of 5min at 0.2 V

M20 after electrolysis of 25min at 0.2 V

M21 after electrolysis of 5min at 0.2 V

M22 after electrolysis of 25min at 0.2 V

TABLE 3
ELECTROCHEMICAL TESTS

3expIT_200.bin 0.2 V

M23 after final CV

TAKEN SAMPLES



- M31 after electrolysis of 30s at 0.2 V
- M32 after electrolysis of 1min at 0.2 V
- M33 after electrolysis of 2min at 0.2 V
- M34 after electrolysis of 5min at 0.2 V
- M35 after electrolysis of 10min at 0.2 V
- M36 after electrolysis of 20min at 0.2 V
- M37 after electrolysis of 40min at 0.2 V



TABLE 4

Sample M3

Main peaks :	7.02	100%	Toluene
	13.43	3.61%	2-etil-hexanol
	14.63	7.01%	2-(2-ethoxyethoxy)-ethanol (<i>instrumental</i>)
	19.36	2.16%	2,5-bis(1,1-dimethylethyl)-phenol
	19.94	1.02%	Diethyl phthalate (<i>rubber</i>)

Sample M5

Main peaks:	13.53	1.55%	Decanal
	14.63	7.01%	2-(2-ethoxyethoxy)-ethanol (<i>instrumental</i>)
	19.37	2.16%	2,5-bis(1,1-dimethylethyl)-phenol

Sample M6

Main peaks:	7.02	6.42%	Toluene
	13.43	4.33%	2-etil-hexanol
	13.53	4.33%	Decanal
	17.49	7.9%	Phenol
	19.37	5.6%	2,5-bis(1,1-dimethylethyl)-phenol



TABLE 5
SAMPLE

M10

M13 CONDITIONS

M14 Baseline solution

M15 0.6 V – 10' PRODUCTS

M16 0.6 V – 25' Traces at very low level of decanal, phenol and derivatives

M17 0.45 V – 5' 12.51 **cycloptanol**
16.87 **1,4-butandiolo**

M18 0.45 V – 25' 12.51 **cycloptanol** (peak of increased height)
16.87 **1,4.butandiolo** (broad peak)

M19 0.3 V – 5' 13.44 **decanal** (traces)
16.87 **1,4-butandiolo**

M20 0.3 V – 25' 13.52 **decanal** (peak of increased height)
16.87 **1,4-butandiolo**

M21 0.2 V – 5' Same peaks as M15 e M16

M22 0.2 V – 25'

0.1 V – 5' 19.37 **phenol, 2-4-bis (1,1-dimetiletil)**

0.1 V – 25' 18.99 **phenol, 2-6-bis (1-metilpropil)**
19.37 **phenol, 2-4-bis (1,1-dimetiletil)** (very high peak)

FIGURE 1

1CV.bin

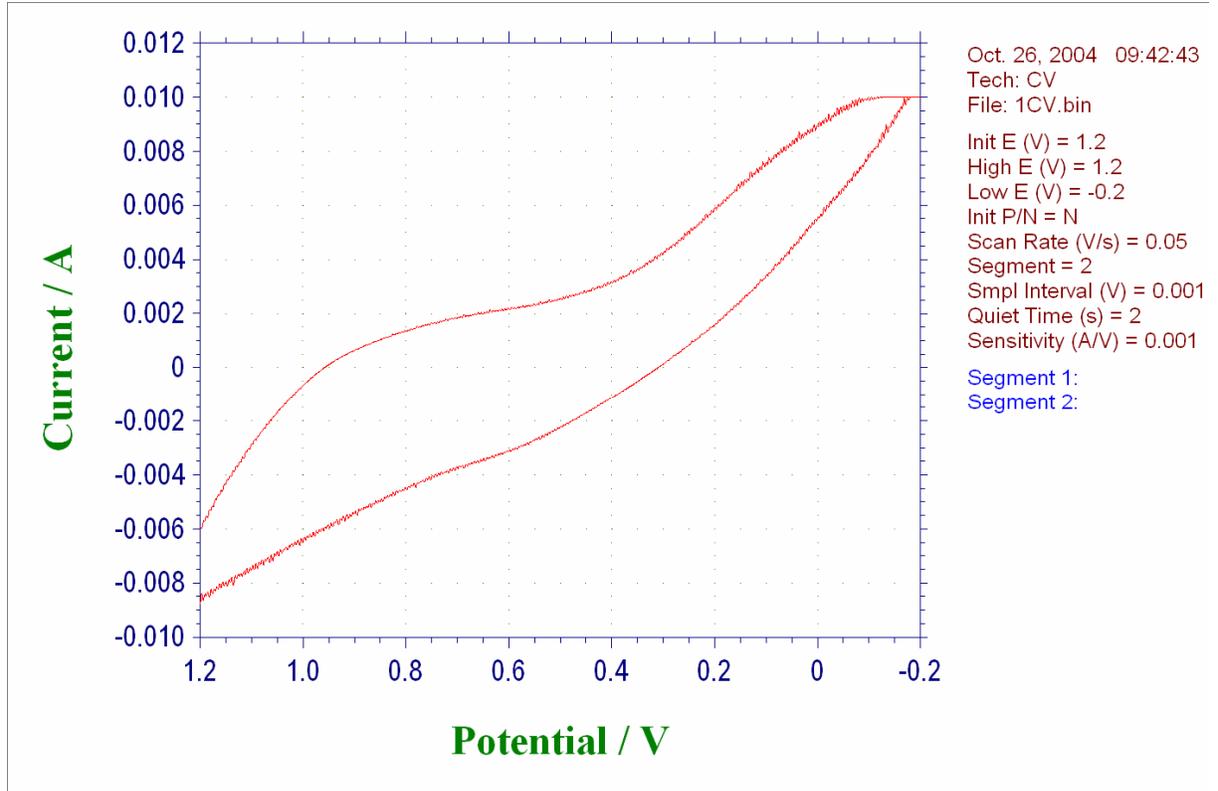
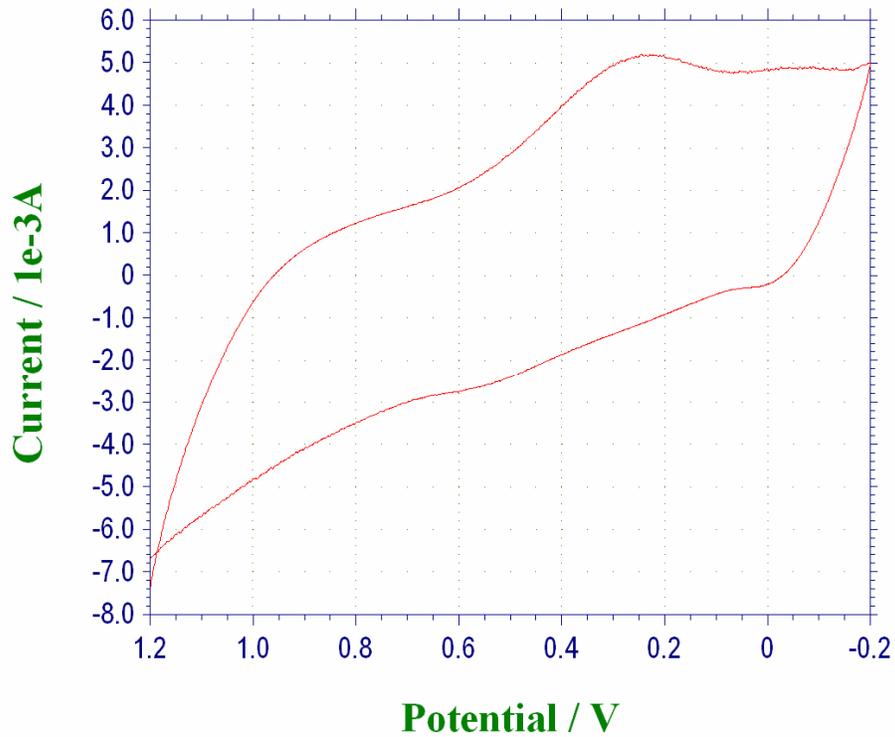


FIGURE 2

11CV.bin



Oct. 26, 2004 09:45:50
Tech: CV
File: 11CV.bin
Init E (V) = 1.2
High E (V) = 1.2
Low E (V) = -0.2
Init P/N = N
Scan Rate (V/s) = 0.02
Segment = 2
Smpl Interval (V) = 0.001
Quiet Time (s) = 2
Sensitivity (A/V) = 0.002
Segment 1:
Segment 2:

FIGURE 3

12CV.bin

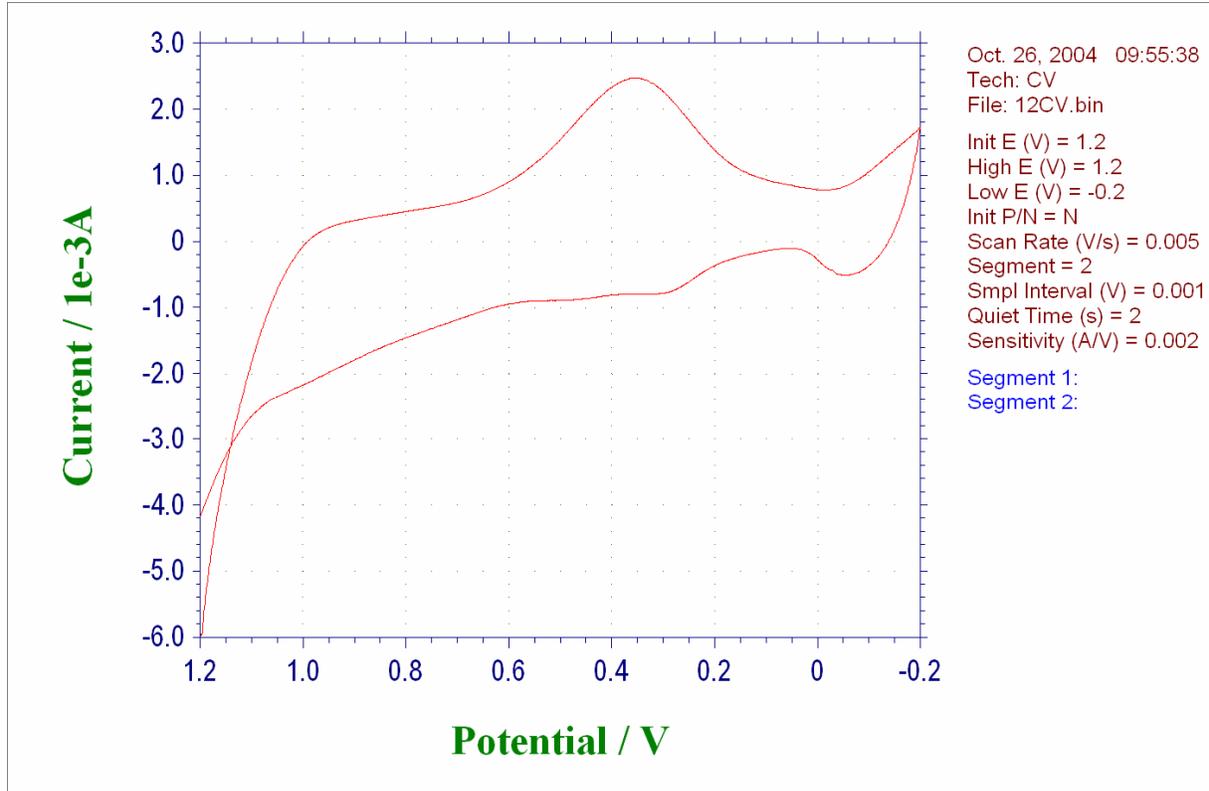


FIGURE 4

13CV.bin

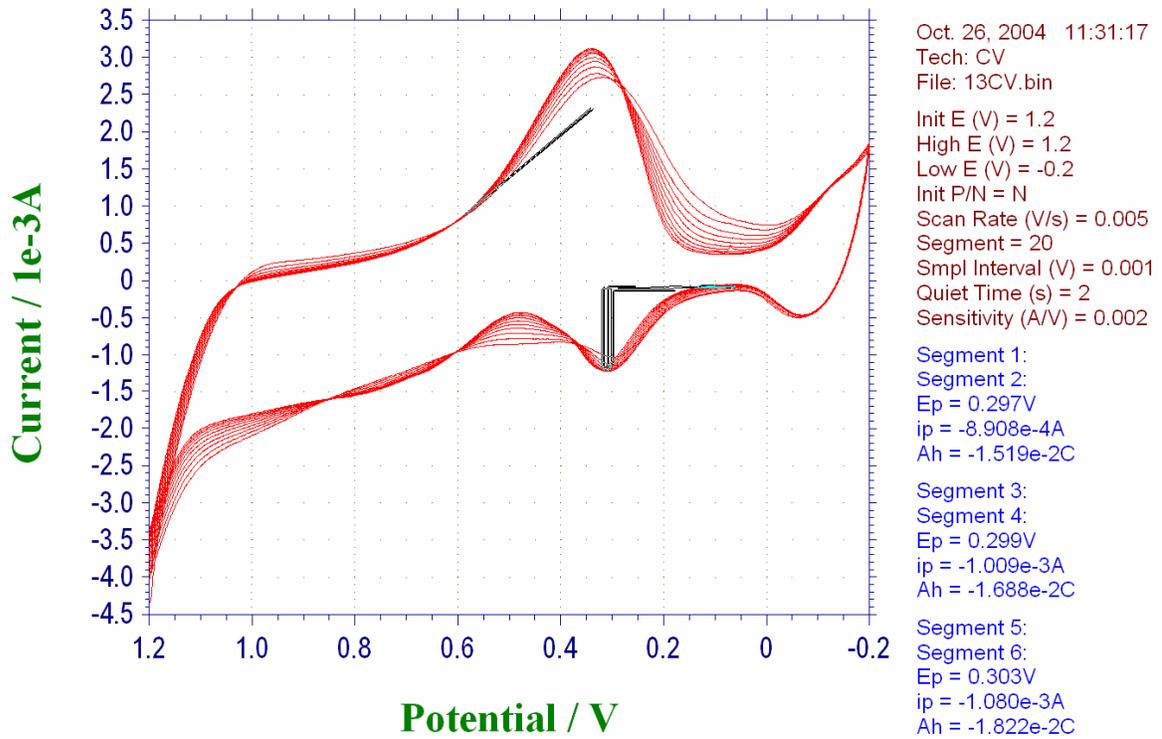


FIGURE 5

Overlay expIT600-200

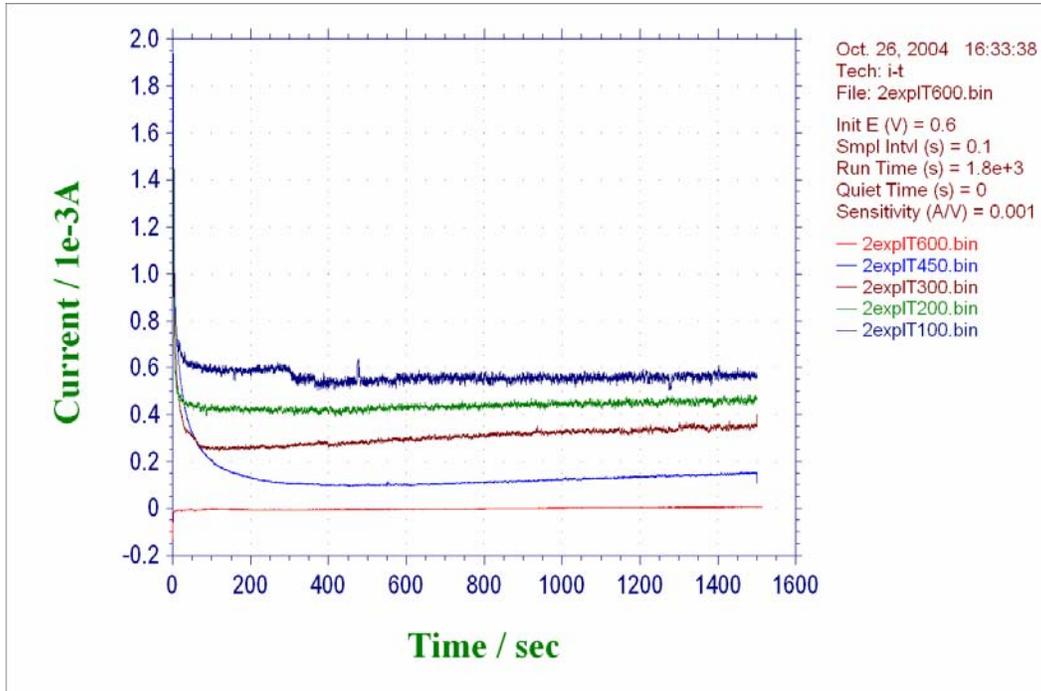


FIGURE6

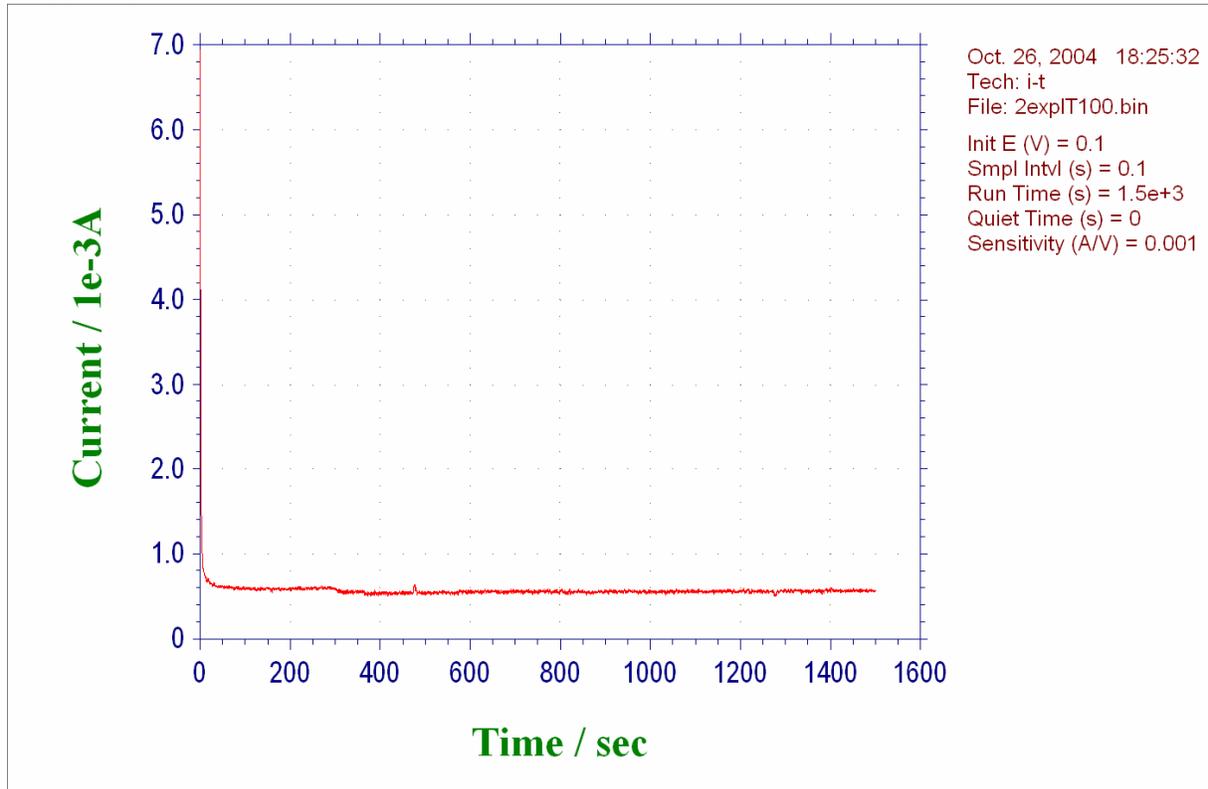




FIGURE 7

3expIT_200.bin

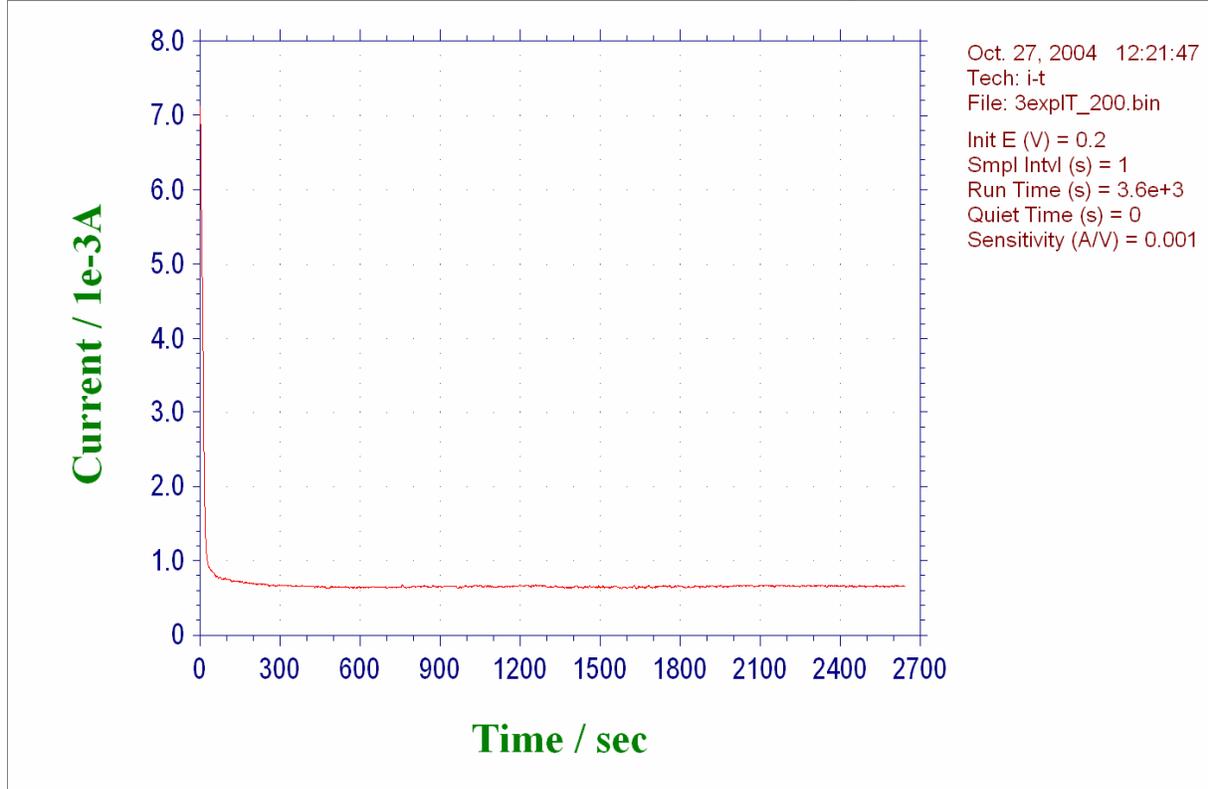


FIGURE 8

3expCVfin.bin

