AN EXPERIMENTAL METHOD TO MEASURE THE RATE OF H(D)-ABSORPTION BY A Pd CATHODE DURING THE ELECTROLYSIS OF AN AQUEOUS SOLUTION: ADVANTAGES AND DISADVANTAGES

M. ALGUERO, J.F. FERNANDEZ, F. CUEVAS AND C. SANCHEZ

Dpto. Física de Materiales, C-IV. Facultad de Ciencias. Universidad Autónoma.
Cantoblanco 28049. Madrid. Spain

Abstract

An experimental set up to measure the rate of H(D) uptake by a Pd cathode during the electrolysis of an aqueous electrolyte has been built and its behavior is analyzed. The experimental procedure is based on the pressure changes that take place within a closed electrolytic cell during the hydride (deuteride) formation. Calibration of the system has been done by accomplishing electrolysis with two Pt electrodes and the error sources have been studied. A protocol to be used in Pd hydrogenation (deuteration) is defined. Finally, the advantages and disadvantages of this experimental method against measurements of the Pd electric resistance variations are briefly discussed.

1. Introduction

It has been shown [1-3] that neither thermal nor nuclear effects are expected during the electrolysis of a heavy water electrolyte with a Pd cathode unless a $D/Pd \geq$ 0.8-0.9 is reached and sustained for a prolonged time, i.e. more than a week. On the other hand, the amount of deuterium that a Pd cathode absorbs, has been shown to depend on both, the characteristics of the electrolysis, i.e. electrolyte, electrodes arrangement, electrolytic current, temperature, etc. and the structural features of the sample bulk and surface [2-5]. Data on the final values of D/Pd with a well established electrolytic configuration and sample metallurgy are scattered and often contradictory [4,5]. It has been also pointed out that once a $D/Pd \geq 0.9$ has been reached it seems to decrease with time during prolonged electrolysis at high current densities [2,4,6].

We have built up an experimental set up to measure the rate of hydrogen (deuterium) absorption by a Pd cathode during the electrolysis of an aqueous solution. The technique deals with the amount of gas evolved during the electrolysis. The pressure in a closed electrolytic cell is allowed to raised up to a fixed value at which an electrovalve is opened and closed. The difference between the number of gas molecules evolved in a period of time, and the number of them that should have been evolved, according to the electric charge that has passed in the same period through the cell, is a direct measure of the H(D) absorbed by the cathode (in absence of other sinks or sources

of gas). Similar set ups have been used successfully by other groups in cold fusion research [5,7].

The experimental set up has been tested by carrying out several electrolyses of a light water electrolyte with two Pt electrodes. The role played by the different parameters relevant to the set up has been defined, as well as a protocol to be used in Pd loading experiments.

2. Experimental

The set up we have built up (Fig.1) comprised a closed electrolytic cell (1), an U-shaped glass manometer (2), a deposit with $CaCl_2$ (3), an electrovalve (4), and an electronic circuit (5) that opens the electrovalve. Later on a pre-deposit of water (6), and a thermostatic bath to control the temperature of the electrolyte (7), were added. At overpressures, ΔP, below a fixed value, ΔP_f, the electronic circuit is opened and the electrovalve is closed. The pressure in the cell raises during electrolysis due to gas evolution. When the overpressure in the cell reaches ΔP_f, the level of mercury in the open arm of the manometer reaches two Pt wires, and close the electronic circuit that opens the electrovalve, what allows the accumulated overpressure to disappear. The level of mercury goes down opening the circuit, and so, closing the electrovalve. The circuit is able to keep the electrovalve opened for a certain time, t_r, after this switching. The time between two openings, t_i, is recorded in a PC. Experimental data collected during an electrolysis are a series of times, $\{t_i\}$.

The number of moles, Δn_o, of both $H(D)_2$ and O_2 needed to increase the pressure in the free volume of the electrolytic cell, V, in ΔP_f, at temperature T is given by eq.(1). On the other hand, the number of moles, Δn, of both $H(D)_2$ and O_2, that are evolved in a period of time, t_i, between two openings of the electrovalve, during an electrolysis accomplished in galvanostatic conditions at current I is given by eq.(2), where N_A is the Avogadro´s number and e the electronic charge.

$$V\Delta P_f = \Delta n_o RT \qquad (1)$$

$$\Delta n = \left(\frac{I}{2 N_A e} + \frac{I}{4 N_A e} \right) t_i \qquad (2)$$

The difference, Δn_i, between Δn and Δn_o, that occurs during an electrolysis accomplished with a Pd cathode, is the number of moles of $H(D)$ that have been absorbed by the cathode in the period t_i. The whole amount of $H(D)$ absorbed during an electrolysis is the sum of the series $\{\Delta n_i\}$. The free volume, V, is not constant during an electrolysis but it diminishes due to the electrolyzed water and so, t_i increases with time in a linear fashion at constant electrolytic current.

3. Results
3.1. Qualitative aspects of the set up
A great number of the electrolyses accomplished were devoted to understand and solve the problems we readily faced.

. Both H_2O and Hg were tested as filling liquids of the manometer. H_2O was not operative because its evaporation. Hg also presented shortcomings. Its surface became oxidized during electrolysis so a small amount of an organic compound was put above the Hg surface to prevent it.

. The linear increase of t_i was bigger than it should be by considering the loss of H_2O by electrolysis. It was also observed that bubbles were often formed in the glass line. Both observations were related to the evaporation of the electrolyte induced by the dessecator ($CaCl_2$). The pre-deposit of water (6) was placed to minimize this effect.

. It was also found that some gases (air, H_2. O_2) were absorbed and released by the electrolyte. These phenomena were specially present at the beginning of the electrolysis and whenever a sharp change of the electrolyte temperature took place. The thermostatic bath was placed to eliminate the second possibility. The electrolyte behavior at the beginning of the electrolysis will be discussed in the next paragraph.

3.2. A quantitative analysis of the initial transients

Following the inclusion of the pre-deposit of water and the thermostatic bath, a more systematic program of measurements was designed. Three sets of electrolyses of a LiOH 0.1M electrolyte using Pt foils as electrodes were done. The whole volume of the system was 2000cc. All the components (Hg, electrolyte, $CaCl_2$, and the water within the pre-deposit) were renewed before each electrolysis. Table 1 summarizes the conditions at which the electrolyses were accomplished. The time the electrovalve (4) remained open after the closing of the circuit (5) was fixed in the three sets as 3.4 s. This time allows a good equilibration of the mercury in the two arms of the manometer (2).

Fig.2 shows $\{t_i\}$ for electrolysis 6. $\{t_i\}$ values fit very well to an expression with 6 parameters of the form $\{a + b\tau_i - c \exp(-d\tau_i) + f \exp(-g\tau_i)\}$, in which τ_i is the electrolysis time at which t_i was recorded. The linear increase is due to the water loss by electrolysis and by evaporation, whenever the pre-deposit is not placed. The two exponential terms describe a transient in t_i that is produced by the release and the absorption of different gases by the electrolyte. The ten electrolyses have been fitted to such an expression and the parameters have been evaluated.

Fig.3 (a) shows the parameter **a** for the ten electrolyses. **a** is the time, t_1, elapsed between switching the current on and the first opening of the electrovalve. It is given by eq.(1-2) with the initial free volume, V=2000cc-V_e. The continous lines in Fig.3 (a) are the expected values according to eq.(1-2). The error bars are the errors associated with the expected values, calculated from the errors of T, V_e, ΔP_f and I. A good agreement is reached between **a** from $\{t_i\}$ and the expected values. This was a essential pre-requisite for the feasibility of the experimental set up. Fig.3 (b) shows the parameter **b**, the slope of the linear increase in t_i. The dashed line in Fig.3 (b) is the expected value of **b** considering only the effect of electrolysis. The pre-deposit was not placed in sets 1 and 3 and **b** from these sets is clearly above the dashed line. The pre-deposit was placed in set 2 and **b** from it is well around the dashed line, so, it is clear the importance of the pre-deposit of water to minimize the effect of electrolyte evaporation.

Fig.4 shows the two parameters, **c** and **d**, of the first initial transient for the ten electrolyses. They do not show a clear dependence on I, although they seems to change with the volume of electrolyte, V_e. This transient is due to a release of gas from some of the components of the system. We have related it to a release of the air solved initially

443

in the electrolyte. This effect strongly depends on the previous history of the aqueous solution.

Fig.5 shows the two parameters of the second initial transient, **f** and **g**, for the ten electrolyses. Both show a clear dependence on I, so it seems that it is likely due to a $H(D)_2$ and O_2 absorption by the electrolyte. The pre-exponential factor, **f**, follows a I^{-1} behavior, as expected in a process that is related to the amount of gas evolved by electrolysis that is solved in the electrolyte. The parameter **g** increases as I increases, i.e. the transient is faster when the gas evolution rate is faster.

Both initial transients must be taken into account in an electrolysis with a Pd cathode. If they are not considered an uncertainty of 5-10% in the evaluation of the mean H(D)/Pd, $\overline{H(D)/Pd}$ is introduced. However the corresponding parameters present a behavior quite irreproducible that makes their evaluation really complicated. Therefore we searched for any procedure to eliminate the initial transients in t_i. We have found that they do not appear if an adequate mixture of $H(D)_2$ and O_2 is bubbled through the electrolyte prior to the electrolysis. A similar conclusion has been reached by other authors [1].

4. Discussion

The evaluation of the amount of H(D) absorbed by the Pd cathode is accomplished by summing all the Δn_i. It is important to be aware that any error in the determination of Δn_o, uncertainties in V_c, or ΔP_f, is repeated in a systematic way in each of the contributions. On the other hand it has been shown that the initial transients must be suppressed by a previous bubbling through the electrolyte. We have accomplished it by locating three Pt electrodes in the closed cell besides the Pd one. A pre-electrolysis is accomplished with two of the Pt electrodes, while the Pd is anodically polarized against the third Pt to avoid its hydrogenation (deuteration) during this step. It allows to avoid the initial transients whether the cell is not opened before the loading experiment and to evaluate "in situ" Δn_o from the series $\{t_i\}$ recorded during the pre-electrolysis.

To finish, the advantages and disadvantages of our experimental set up and related ones, either sealed cells with recombination catalyzers [3] or cells that are dinamically opened and closed [5,7], against electric resistance measurements are briefly discussed.

A main disadvantage of this set up, which is not presented by resistance measurements, appears in relation to its use in "Excess Heat" measurements: its strong response to changes of temperature in the electrolyte. A sharp change in temperature produces a release (whether T increases), or an absorption (whether T decreases) of gases from or by the electrolyte. A calibration of this effect is needed to avoid an uncertainty of a few % in the evaluation of the $\overline{H(D)/Pd}$ during an "Excess Heat" experiment.

It presents two clear advantages against resistance measurements. (1) It has been pointed out [8] that the relation $\rho(H(D)/Pd)$, where ρ is the resistivity, changes significantly from one sample to another. Moreover, these relations can change in a unique sample whether it suffers irreversible structural changes during its loading. It is

well known that the electric resistance presents hysteresis during sequential loadings and deloadings. The $\overline{H(D)/Pd}$ evaluation from measurements of gas evolution is not affected by the structural properties of the cathodes. (2) ρ measurements do not give the $\overline{H(D)/Pd}$ as a function of the electrolysis time, but they only give a final value, when a stationary situation has been reached. It has been shown in [4,9] that the existence of gradients of H(D) in the Pd cathode do not allow a proper evaluation of $\overline{H(D)/Pd}$ from ρ. In contrast, the set up in our lab allows to obtain $\overline{H(D)/Pd}$ vs. t curves during the electrolysis, and so, to make a study of the rates of H(D) absorption by Pd. This is likely the main advantage of volumetric techniques since published data on rates of H(D) absorption during electrolysis of aqueous solutions with Pd cathodes are even more scattered than data on final H(D)/Pd, when a stationary situation has been reached.

5. Conclusions

It has been tested an experimental set up to measure the rate of H(D)-absorption by a Pd cathode during the electrolysis of an aqueous solution. It has been shown that some cautions proposed in this paper must be taken. The set up allows not only to measure final H(D)/Pd, but to record $\overline{H(D)/Pd}$ vs. t curves during electrolysis.

6. Acknowledgments

7. References

[1] K. Kunimatsu, N. Hasegawa, A. Kubota, N. Imai, M. Ishikawa, H. Akita and Y. Tsuchida. "Frontiers of Cold Fusion", ed. H. Ikegami. Universal Academy Press inc. Tokyo (1993). 31-45.

[2] M.C.H. McKubre, S. Crouch-Baker, R.C. Rocha Filho, S.I. Smedley, F.L: Tanzella, T.O. Passell and J. Santucci. J. Electroanal. Chem., 368 (1994) 55-66.

[3] F.G. Will, K. Cedzynska and D.C. Linton. J. Electroanal. Chem. 360 (1993) 161-176.

[4] T.A. Green and T.I. Quickenden. J. Electroanal. Chem. 368 (1994) 121-131.

[5] S. Nezu and T. Sano. Transactions of fusion tech. 26 (Dec.1994) 69-73

[6] K. Ota, H. Yoshitake, A. Yamazaki, M. Kuratsuka, K. Yamaki, K. Ando, Y. Iida and N. Kamiya. Transactions of fusion tech. 26 (Dec.1994) 138-142.

[7] F. Celani, A. Spallone, P. Tripodi, A. Nuvoli, A. Petrocchi, D. di Gioacchino, M. Boutet, P. Marini and V. di Stefano. Transactions of fusion tech. 26 (Dec.1994) 127-137.

[8] B. Baranowski, S. Filipek and W. Raczynski. Polish J. Chem., 68 (1994) 845-857.

[9] M.C.H. McKubre, S. Crouch-Baker, A.M. Riley, R.C. Rocha Filho, M. Schreiber, S.I. Smedley and F.L: Tanzella. Electrochemical Society Proceedings, Vol. 92-5, 269-286.
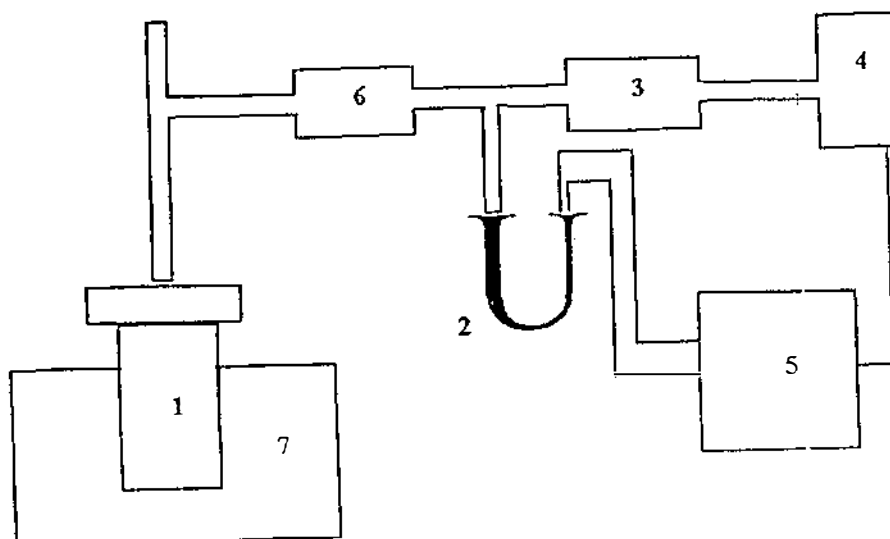
Fig.1 (1) Closed electrolytic cell. (2) U-shaped glass manometer. (3) deposit with $CaCl_2$. (4) electrovalve. (5) electronic circuit. (6) pre-deposit of water. (7) thermostatic bath

TABLE 1

Run	Set	t_e (h)	V_e (cc)	ΔP_f (torr)	T_e (K)	I (mA)
1	1	45	600±6	6.18±.06	294±1	400±1
2	1	45	600±6	6.18±.06	294±1	600±1
3	1	80	600±6	6.18±.06	294±1	800±1
4	2	24	1500±15*	7.16±.06	285±1	200±1
5	2	36	1500±15*	7.16±.06	285±1	400±1
6	2	20	1500±15*	7.16±.06	285±1	600±1
7	2	20	1500±15*	7.16±.06	285±1	800±1
8	3	50	1500±15*	6.189±.006	294±1	400±1
9	3	24	1500±15*	6.189±.006	294±1	600±1
10	3	45	1500±15*	6.189±.006	294±1	800±1

Table 1. t_e: time of electrolysis. V_e: volume of electrolyte. In electrolysis marked as * the electrolyte was stirred. ΔP_f: fixed overpressure. T_e: electrolyte temperature. I : electrolytic current. The pre-deposit of water was not placed in sets 1 and 3.
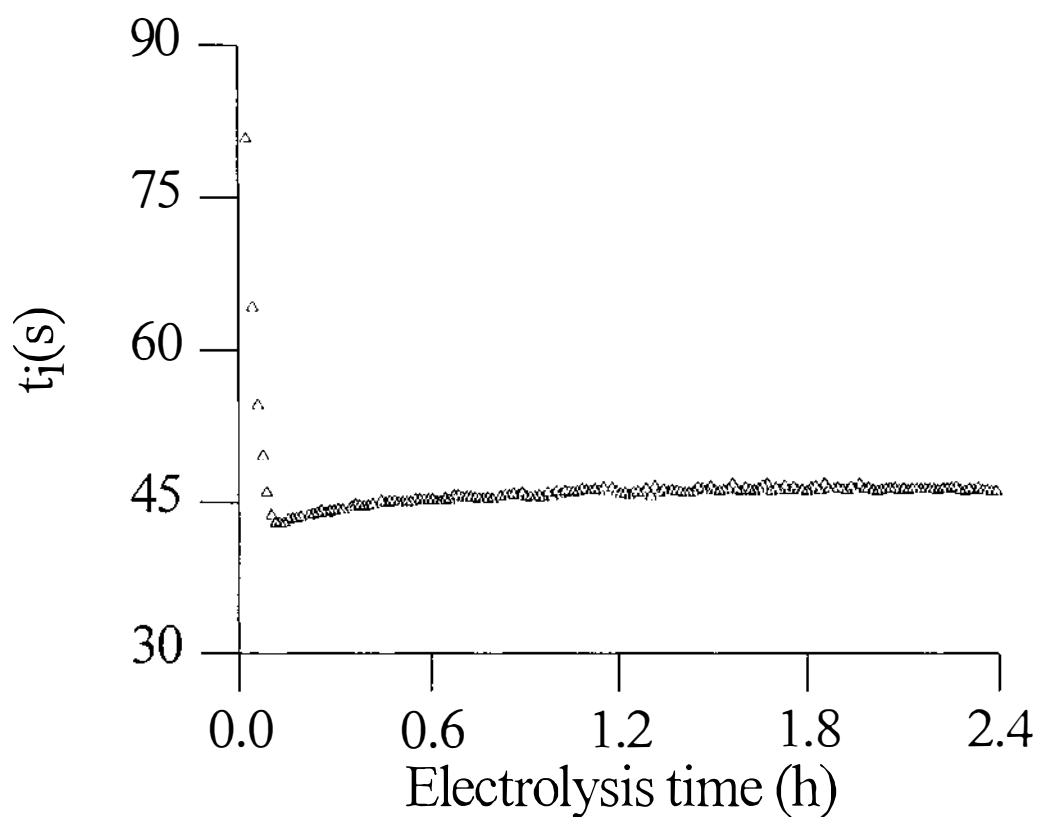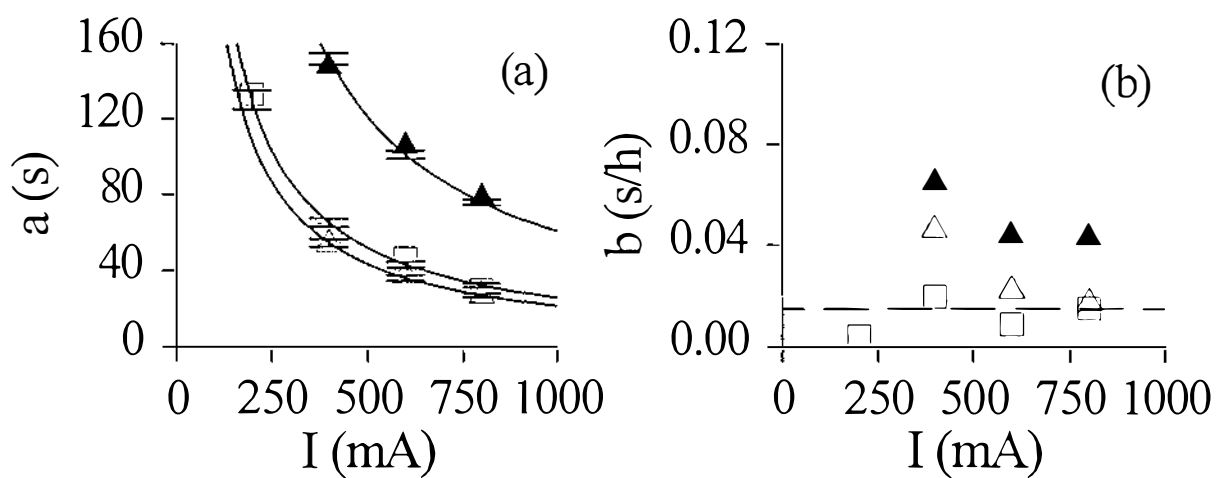
Fig.2 (t_i) in electrolysis 6. 2.4 first hours

Fig.3 (a) a from the fittings of the 10 electrolyses. (b) b from the fittings of the 10 electrolyses. Set 1: black triangles. Set 2: open squares. Set 3: open triangles. The pre-deposit of water was not placed in sets 1 and 3
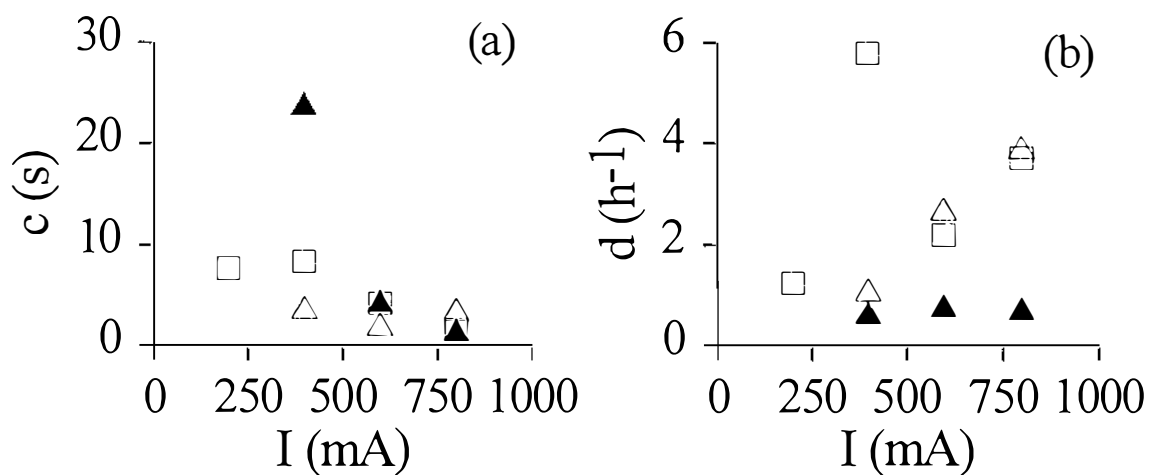
Fig.4 (a) c from the fittings of the 10 electrolyses. (b) d from the fittings of the 10 electrolyses. Set 1: black triangles. Set 2: open squares. Set 3: open triangles
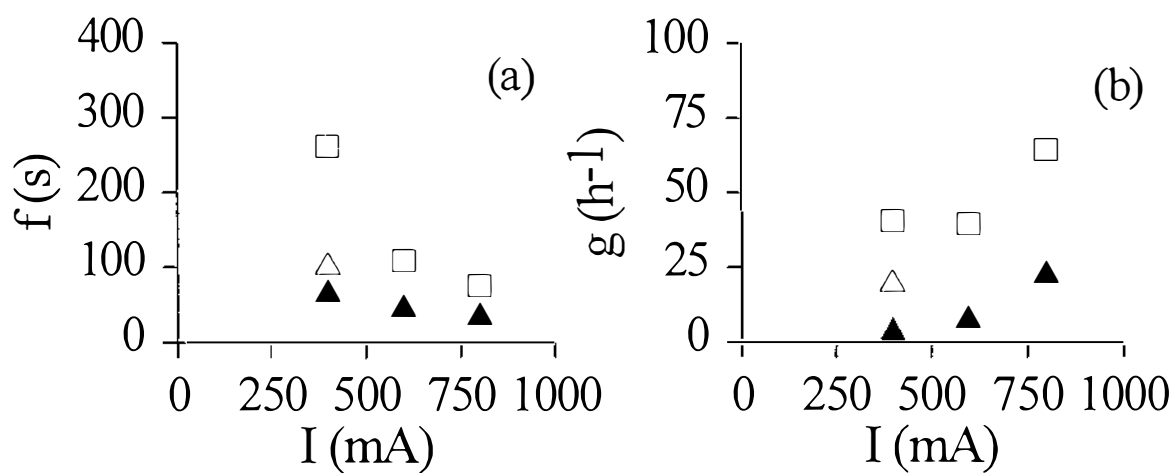

Fig.5 (a) f from the fittings of the 10 electrolyses. (b) g from the fittings of the 10 electrolyses. Set 1: black triangles. Set 2: open squares. Set 3: open triangles