

Mariela E. Sola · Horacio G. Rotstein · Julio C. Bazán

The Ag(s)/AgI(s)/graphite solid cell as iodine sensor: speed of response and use of Cs-doped AgI as electrolyte

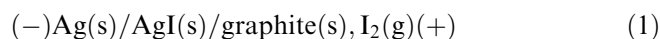
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Abstract The time response of a Ag(s)/AgI(s)/graphite(s), I₂(g) galvanic cell as iodine sensor was studied using both pure AgI and CsI doped AgI as electrolyte. The use of doped silver iodide expanded considerably the working temperature. An analytical modeling of the sensor response is presented.

Keywords Silver iodide · Iodine sensor · Doped electrolyte · Time response

Introduction

It is already well known [1, 2, 3] that a galvanic formation cell like



may be used as iodine sensor due to the fact that, in the range of stability of the α -AgI phase at $T > 420$ K, the cell potential follows the Nernstian relationship with the iodine partial pressure:

$$E = E^\circ + (RT/2F)\ln P_{\text{I}_2} \quad (2)$$

the cell reaction being



As the silver ions are the only mobile ionic species, they migrate from the anode to the cathode, where the formation reaction takes place. The corresponding cathodic and anodic electrode reactions were studied in our laboratory [4, 5, 6]. However, for the β -AgI phase under 420 K, a partial electronic conductivity appears which increases with the iodine partial pressure [1] and would lead to deviations from the Nernstian behavior. In this way, a limitation on the application of the sensor arises for temperatures lower than that of the α - β AgI transition. On the other hand, in spite of the extended interest in this type of gas sensors for a variety of applications [7, 8, 9, 10] there is not much information about the speed of response of such electrochemical devices. In this communication there is a report on an attempt to ascertain the parameters affecting the speed of response of that electrode by proposing a mathematical model. Besides, based on the previously reported finding that doping AgI with up to 6 mol% CsI decreases considerably the α - β transition temperature [11] maintaining at the same time the high level of conductivity associated with the α -AgI structure, CsI doped AgI was used as electrolyte instead of pure AgI. In that way a considerable expansion of the working temperature range of the sensor towards lower temperatures was attained.

Experimental

A graphite disk of about 0.5 cm diameter was used as working electrode and a silver disk of about 1 cm diameter as both counter and reference electrode, as schematically shown in Fig. 1. The electrolyte was either pure or 6 mol% CsI doped silver iodide, in form of pellets of 0.7 cm in diameter and between 0.09 cm and 0.20 cm in thickness. The AgI was synthesized from AgNO₃ and KI both of p.a. quality. Cesium iodide was Cerac 99.99%. The amount of Cs in the doped sample was analyzed by atomic absorption spectrography. The time response of the cell potential was measured by suddenly putting the working electrode into contact with a fixed partial pressure of iodine. This was performed by breaking a glass bulb, which initially isolated the electrode from the gaseous environment. The voltage-time measurements were performed by means of a high impedance digital voltmeter connected to a pen recorder. The working iodine pressures ranged from 39 Pa

Julio C. Bazán, Research Fellow, CIC Prov. Buenos Aires, Argentina

M.E. Sola · J.C. Bazán (✉)
Departamento de Química e Ingeniería
Química, Universidad Nacional
del Sur, 8000 Bahía Blanca, Argentina
E-mail: jcbazan@criba.edu.ar

H.G. Rotstein
Volen Center for Complex Systems,
Brandeis University, Waltham,
MA 02454-9110-USA

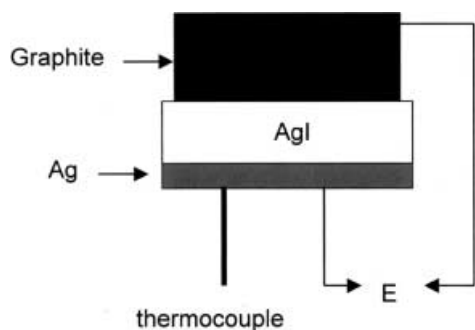


Fig. 1 Schematic view of the I_2 sensor

to 519 Pa (from 3.9×10^{-4} atm to 5.1×10^{-3} atm) at temperatures between 373 and 443 K.

Results and discussion

Pure AgI as electrolyte

Figures 2 and 3 show the response of the sensor under different working conditions, in the temperature range of α -AgI. The ordinate shows the ratio E_t/E between the observed potential at time t and the calculated Nernstian potential at the working conditions. Initially a steep rise up to about 96% of the theoretical value is observed, followed by a slower variation. The final value at longer times reached about 99% of the expected one. This behavior agrees with results reported for similar systems [7, 8]. It is to be noted that the value of the initial cell potential is higher for the samples previously exposed to iodine, as shown in Fig. 2. In the stability range of the low temperature β -AgI phase the cell response follows a similar but slower pattern, as seen in Fig. 4. No influence of the pellet thickness was observed. It is worth noting that the different silver ion conductivities (i.e., diffusivities) between the α and β phases of AgI, which is of about four orders of magnitude, does not reflect upon the speed of response of both phases of the electrolyte.

CsI doped AgI as electrolyte

It is to be mentioned that in this case the cell equilibrium potential is somewhat lower than that of the cell with pure AgI as electrolyte, as was determined in previous work [12]. Figure 5 shows the potential-time curves of the cell at two different iodine partial pressures and at a temperature in which the pure electrolyte would be in its β -phase. It is to be noted that a curve for the cell with doped electrolyte at $P_{I_2} = 55$ Pa is also included in Fig. 4, making it evident that in this case the sensor response is faster in comparison to pure β -AgI. As expected, the doped electrolyte behaves like the pure electrolyte in its α -phase.

As found earlier, the electrode process at the interface $AgI/I_2(g)$, C_{graphite} is controlled by adsorption and recombination steps at short times [4], while it is con-

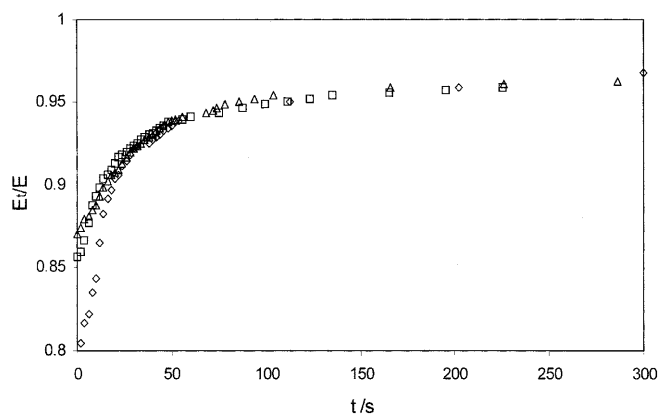


Fig. 2 Transient response of E_t/E , $T = 443$ K, iodine partial pressure = 55 Pa, for three consecutive runs. Increasing initial E values reflect previous exposure to iodine

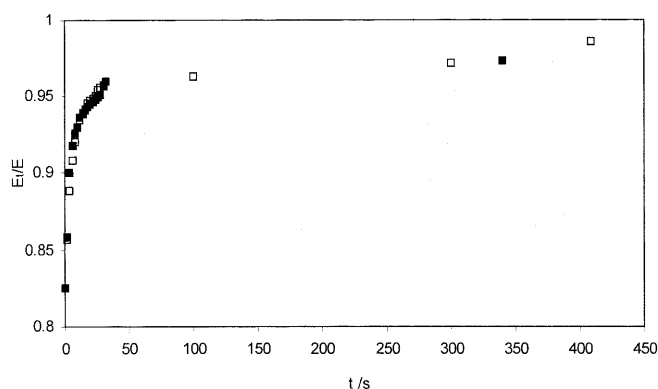


Fig. 3 Transient response of E_t/E , $T = 443$ K: (open squares) iodine partial pressure = 121.5 Pa; (filled squares) iodine partial pressure = 280 Pa

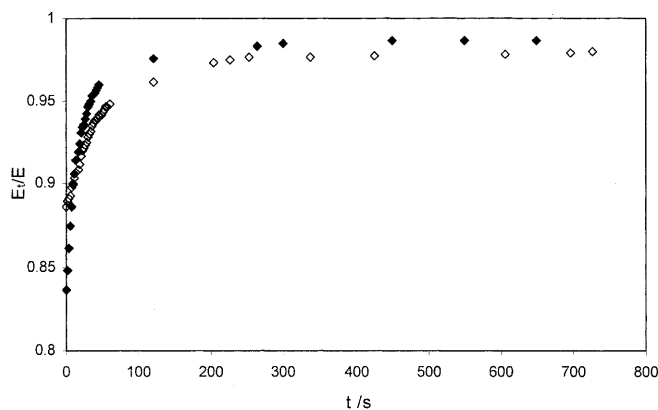


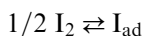
Fig. 4 Transient response of E_t/E ; (open diamonds) β -AgI, $T = 393$ K, iodine partial pressure = 55 Pa; (filled diamonds) CsI doped AgI, $T = 393$ K, iodine partial pressure = 55 Pa

trolled by a diffusion step at longer times [5]. Consequently the behavior observed might be explained by a first adsorption step followed by a diffusion step.

Modelling the electrode time response

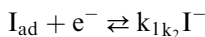
To get an analytical description of the sensor time response when exposed to a certain iodine partial pressure, the total process to consider is that of iodine incorporation from the gas phase into solid AgI, which may be assumed to occur through the following steps:

1. Diffusion from the gas phase up to the solid surface
2. Adsorption of iodine on the silver iodide surface



followed by

3. Built in the surface ionic network



and

4. Internal diffusion of I^- into the solid

The first step may be assumed as faster than the other two, due to the high diffusion coefficient of iodine in the gas phase (about $8.3 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$).

It may be assumed that equilibrium is reached for step II which may be expressed by

$$K_{ad} = [I_{ad}]/P^{1/2} \quad (4)$$

where P is the iodine partial pressure. This is reasonable in view of the relatively large time required for complete stabilization, which points to a predominance of the diffusion step.

Thus, using Eq. (4) and making $K_1 = k_1 K_{ad}$ step 3 may be described by

$$d[I^-]/dt = k_1 [I_{ad}] - k_2 [I^-] = K_1 P^{1/2} - k_2 [I^-] \quad (5)$$

In order to solve the mathematical problem, Eq. (4) is written as

$$dC/dt = K_1 P^{1/2} - k_2 C \quad (6)$$

where $C = [I^-]$.

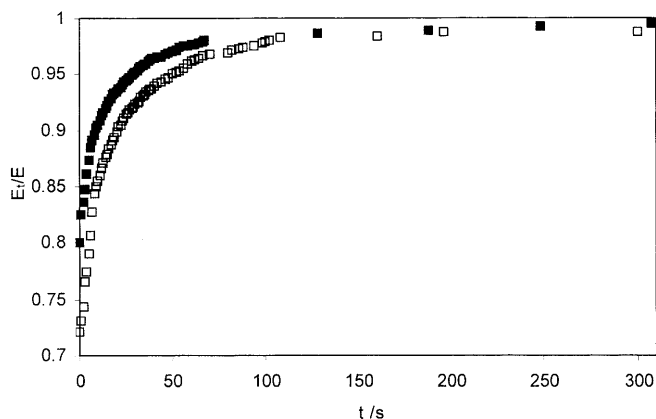


Fig. 5 Transient response of E_t/E , CsI doped AgI: (open squares) iodine partial pressure = 104 Pa, $T = 376 \text{ K}$; (filled squares) iodine partial pressure = 426 Pa, $T = 376 \text{ K}$

The diffusion step 4 was considered as occurring radially from the border to the center of the pellet, which seems to be a reasonable two-dimensional assumption taking into account the system geometry and the absence of noticeable effect of the pellet thickness. This is schematically shown in Fig. 6. Introducing a variable U which describes the iodide concentration along r in the pellet, so as to differentiate from C which represents the iodide concentration at the border of the pellet, this step could be described by the corresponding form of the second Fick's law:

$$\begin{aligned} U_t &= D[U_{rr} + 1/r U_r] & r \leq r_0, t > 0 \\ U(r, 0) &= C_0 & r < r_0 \\ U(r_0, t) &= C(t) & t \geq 0 \end{aligned} \quad (7)$$

where U_t is the derivative of U with respect to time, and U_r and U_{rr} are the first and second derivatives of U with respect to the radius. D represents the diffusion coefficient of iodide into the silver iodide pellet; r_0 the silver iodide pellet radius. Thus $U(r, 0)$, i.e., before the start of the diffusion process is equal to C_0 the initial iodide concentration in the pellet, assumed as constant for each run and $U(r_0, t)$ is equal to $C(t)$ the iodide concentration at the pellet border.

To solve the problem it is necessary to incorporate the solution of Eq. (6), which is given as

$$C(t) = (K_1 P^{1/2})/k_2 + (C_0 - K_1 P^{1/2}/k_2) \exp(-k_2 t) \quad (8)$$

Thereafter the variable W is introduced, which is defined by

$$W(r, t) = U(r, t) - C(t)$$

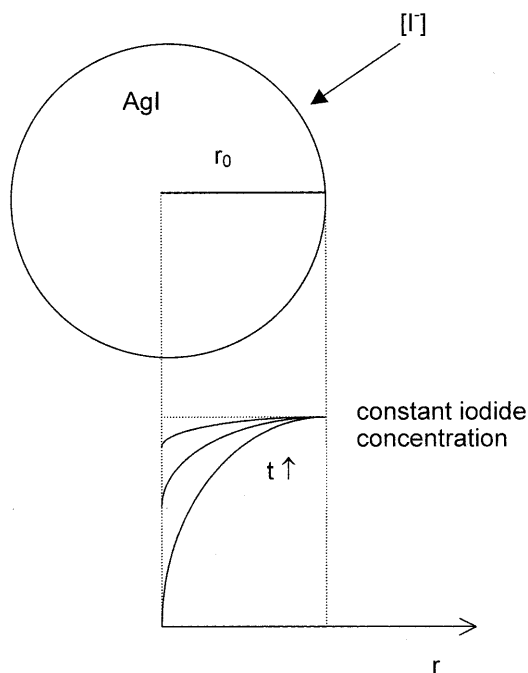


Fig. 6 Schematic diffusion path

that is, W is a measure of the iodine equilibration in the pellet, its value being zero both at the beginning and at the end of that process. With that, the diffusion problem may be written as

$$\begin{aligned} W_t &= D[W_{rr} + 1/r W_r] - C_t & r \leq r_o, t > 0 \\ W(r, 0) &= 0 & r < r_o \\ W(r_o, t) &= 0 & t \geq 0 \end{aligned} \quad (9)$$

where the subscripts indicate the same derivatives as above. This equation represents the change with time of the difference between the iodide concentration along the pellet radius and at the border of the same pellet.

This system was solved by the classical method of variable separation using zeroth order Bessel functions so that $W(r,t)$ is expressed by Fourier-Bessel series in which the time dependence is exponentially decreasing, i.e., $W(r,t)$ tends towards zero as time tends to infinity. Finally, the solution of Eq. (7) is given by

$$U(r, t) = W(r, t) + C(t) \quad (10)$$

In order to proceed to fit the experimental data to Eq. (10) it may be assumed that in each volume element along the diffusion profile a local equilibrium is reached. In this way, according to Eq. (2), the experimental difference $E_t - E$ between the cell potential at time t and that of the final equilibrium should be proportional to the logarithm of the square root of the corresponding pressures $(P_t/P)^{1/2}$. Furthermore, taking into account the proportionality expressed by Eq. (4) the same relationship should exist between $E_t - E$ and $\ln([I^-]_t/P)^{1/2}$, which is obtained from Eq. (10). Thus, both sets of values should exhibit the same dependence with time. According to that reasoning, the fitting was made by adjusting the calculated $([I^-]_t/P)^{1/2}$ values to the experimental $(P_t/P)^{1/2}$ ones both as a function of time, as shown in Fig. 7a–c. The data were taken starting with a fresh AgI tablet, at $P = 55$ Pa and $T = 443$ K. The a, b, c sequence corresponds to consecutive runs presented to emphasize the influence of the previous exposition to iodine. Figure 8a–c shows similar fittings for Cs-doped AgI, at the same iodine partial pressure, but different temperatures. The corresponding fitting constants are given in Table 1. The fitting parameters are reasonably constant in spite of the different initial potentials. The high value of the diffusion constant of the order of $10^{-3} \text{ cm}^2 \text{ s}^{-1}$ as compared to known values of the diffusion coefficient of iodide ions in AgI, which are about $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ [13] may be explained as a consequence of (a) the approximations made in the model, (b) the fact that the final potential values are not 100% of the theoretical ones, and (c) the existence of some type of coupling between the iodide ion and electronic and/or atomic defects which together with some contribution along grain boundaries would improve the iodide ion movement. These points support the consideration of D as diffusion constant instead of as a conventional diffusion coefficient.

Higher values of the rate constants are obtained for the cell with doped electrolyte, as expected from its faster response. That finding may be explained by assuming that the dopant increases the number of surface active sites for adsorption, as well as improves diffusion by providing new paths along grain boundaries.

Conclusions

It was found that (a) the higher the iodine pressure, the faster the cell response, (b) previous contact with iodine improves its performance, and (c) using the doped electrolyte extends the useful temperature range towards lower values, thus avoiding deviations from Nernstian

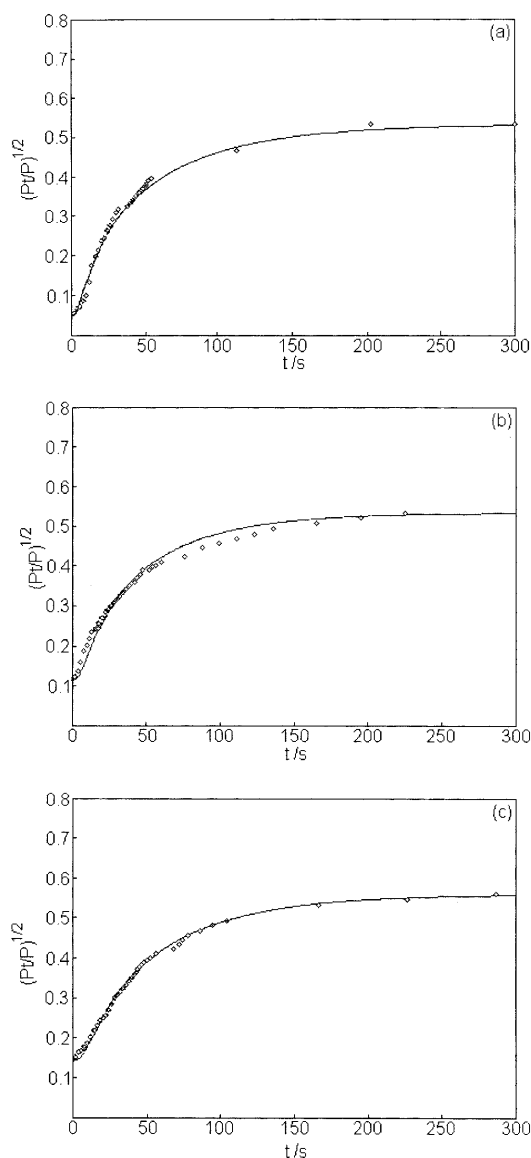


Fig. 7a–c Fitting of the calculated values to the experimental ones as a function of time for data shown in Fig. 2. Initially E values in consecutive runs increase according to previous exposure to iodine: (open diamonds) experimental; (dashed lines) theoretical

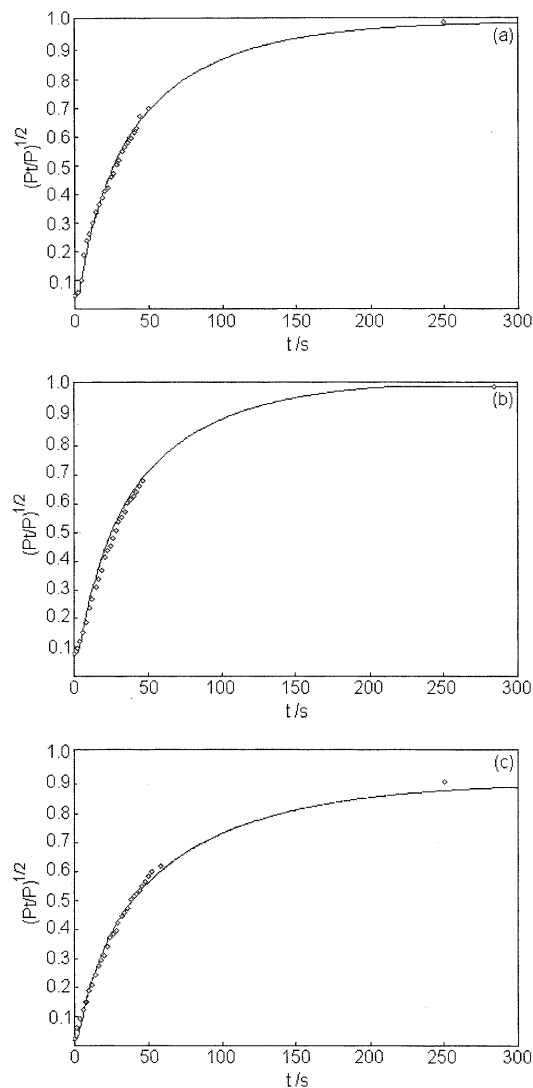


Fig. 8a-c Fitting of the calculated values to the experimental ones as a function of time for Cs-doped AgI, iodine partial pressure = 55 Pa. (open diamonds) experimental; (dashed lines) theoretical: **a** T = 403 K; **b** T = 393 K; **c** T = 385 K

behavior which may arise when using the β -AgI electrolyte.

It is shown that the sensor time response may be modeled on the basis of a sequence of steps involving

Table 1 Fitting constants

AgI	Curve	T/K	P_{I_2}/Pa	k_2/s^{-1}	$D/\text{cm}^2 \text{s}^{-1}$	K_1/s^{-1}
Pure	a	443	55	0.015	0.0040	0.00010
	b	443	55	0.018	0.0037	0.00012
	c	443	55	0.015	0.0030	0.00011
Doped	a	403	55	0.015	0.0045	0.00019
	b	393	55	0.015	0.0045	0.00020
	c	385	55	0.011	0.0045	0.00011

dissociative adsorption of iodine followed by diffusion of iodide ions into the solid electrolyte.

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