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Gaseous Iodine Absorption by a Solid Electrolyte. X-ray Characterization

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Abstract

Gaseous iodine was absorbed by $Ag_7PO_4I_4$ *powder producing its chemical decomposition in around 200 h. The original compound decomposition and the appearance of AgI were followed by quantitative X-ray diffraction. The gravimetric and X-ray diffraction results show a linear relation with the square root of time* ($t^{1/2}$). *According to experimental data the stoichiometry of the reaction is:*

$$Ag_7PO_4I_4(s) + yI_2(g) \rightarrow 4\beta\text{-}AgI(s) + \{Ag_3PO_4 + yI_2\}(s)$$

1 Introduction

The crystalline compound $Ag_7PO_4I_4$ (henceforth API) has high ionic conductivity ($\sigma_i = 1{\cdot}7\ Sm^{-1}$)[1,2] and a low electron transport number ($t_{el} = 2{\cdot}3 \times 10^{-4}$),[1] characteristics which make it potentially interesting for use in solid state electrochemical cells. Its use in iodine sensor devices of the type $Pt/Ag/Ag_7PO_4I_4/I_2(g, p_{I_2})$, C/Pt, shows a shift in the FEM with respect to the thermodynamic values.[1] The cause of this shift from the theoretical values was associated with instability of API in the presence of the gas to be sensed. API possesses a very high absorptive capacity of $I_2(g)$, which produces subsequent decomposition of the absorbent compound[2] (yielding β-AgI as an X-ray detectable product).

The $I_2(g)$ absorption isotherms in an atmosphere of very low humidity content ($p_{H_2O} = 7 \times 10^{-2}$Pa) together with X-ray quantitative diffraction studies showed kinetics that are governed by diffusion in the first stage.[3]

In this paper advances are made in interpreting the chemical reaction during the decomposition process of API, obtaining the probable reaction stoichiometry by analysing the temporal variations in the diffraction peak intensities of API and β-AgI as an X-ray detectable product. Preliminary studies of iodine absorption by Ag_3PO_4 are also presented in order to interpret the API decomposition.

Finally a possible stoichiometry is proposed for the decomposition of API in the presence of gaseous iodine.

2 Experimental

2.1 API preparation and characterization

API was prepared starting from an stoichiometric mixture of AgI (Aldrich 99·999%) and Ag_3PO_4 (Fluka Chem. Puriss.) in a glass ampoule, and bringing the components to fusion for 40 h at 400°C and subsequent fast cooling.[2,3]

The product was then characterized by X-ray diffraction. The components Ag, P and I, were in a stoichiometric concentration as was verified by EDAX.

A conductivity of $\sigma_i = 1{\cdot}7 Sm^{-1}$ and an activation energy value of $E_a = 20{\cdot}26\,kJ\,mol^{-1}$ at 20°C were obtained by the Impedance Method, values which concurred with those of other authors.[4,5]

Melting point, with API decomposition[1–3] was measured, and agreed with Takahashi *et al.*[4]

2.2 Preparation of β-AgI

AgI (Aldrich 99·999%), ground and sifted, was submitted to repeated thermal cycling[6] to obtain the phase change from the mixture β, γ-AgI to β-AgI. The product was characterized by X-ray diffraction.

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2.3 Iodine gas source

Iodine, Mallincrodt A.R was bisublimed on CaO for use as an iodine gas source.

2.4 Obtaining of the I_2 (g) absorption isotherms

Ground and sifted API and Ag_3PO_4 (Fluka Chem. Puriss.) were placed in separate dryers in presence of solid iodine. Humidity was controlled by $Mg(ClO_4)_2$, keeping the whole in darkness to avoid photochemical reactions. The sample weight variations were recorded periodically, making sure the environment was kept free of humidity.

2.5 Obtaining of X-ray diagrams for $\{API+I_2\}$ and $\{Ag_3PO_4+I_2\}$ samples

The area of API and AgI maximum-peak were evaluated for CuK_α X-ray diagrams of $\{API+I_2\}$ samples (obtained as in Section 2.4) for different iodine exposure times. The respective peak areas were calculated using Philips PC-APD software.

Debye-Scherrer Cu-K_α X-ray diagrams on $\{Ag_3PO_4+I_2\}$ samples were also produced for evaluation of the decomposition products.

3 Results and discussion

3.1 $\{API+I_2\}$ samples

In Fig. 1 the area of maximum peak intensity for API is represented versus the square root of the normalized exposure time to iodine ($\tau = t/t_f$, with t_f= 200 h, which is the time necessary for API to disappear). The experimental points correspond to the following equation:

$$I_A = a_A + b_A.\tau^{1/2} \qquad (1)$$

Where $a_A = (54{\cdot}7 \pm 2{\cdot}5)u$ and $b_A = -(54 \pm 5)u$

In (1) the subscript '$_A$' means 'API', and 'u' is the integrated intensity unit (Counts.degree).

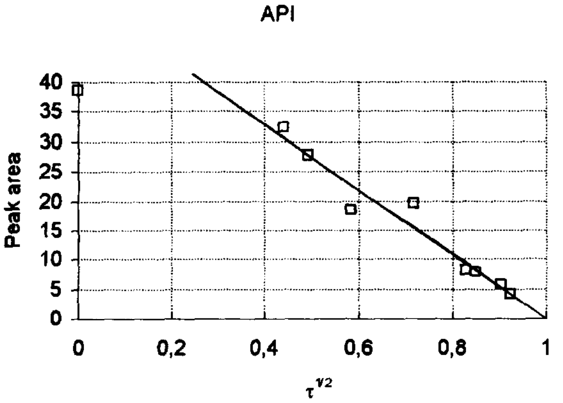

Fig. 1. Obtained areas of maximum peak intensity for API versus normalized exposure time to iodine.

In the same way, the area of maximum peak intensity for AgI was evaluated versus $\tau^{1/2}$ (Fig. 2). It answers to the following equations:

$$I_\beta = a_\beta + b_\beta.\tau^{1/2} \qquad (2)$$

where $a_\beta = (-15 \pm 6)u$ and $b_\beta = (55 \pm 9)u$

In eqn (2) the subscript 'β' means 'β-AgI'.

In Fig. 3 the first part of the gravimetric sorption experiences of iodine by API powder can be observed. The experimental points were adjusted by means of:

$$x = \frac{n_{I2}}{n_A^0} = a_I + b_I.\tau^{1/2} \qquad (3)$$

where a_I=(−0·11 ± 0·05) mol I_2/mol API and b_I=(0·89 ± 0·04) mol I_2/mol API. In eqn (3) the subscript 'I' means 'iodine', n_{I_2} is the mol number of absorbed molecular iodine and n_A^0 is the initial mole number of API.

In the $\beta - AgI$ diagram obtained in Section 2.2, the maximum peak area was measured giving $I_\beta^0 = 68{\cdot}60u$.

3.2 $\{Ag_3PO_4+I_2\}$ samples

Figure 3 also exhibits the first part of the gravimetric sorption isotherm of iodine by Ag_3PO_4 powder. X-ray studies of this sample show that the decomposition products are AgI, and some lines that could not be determined. The values obtained for the interplanar distances are shown in Table 1.

3.3 Discussion

The integrated intensity obtained by X-ray diffraction for a given peak from a given crystalline substance 'i' can be expressed as:[7]

$$I_i = \frac{K_i.C_i}{\mu_m} \qquad (4)$$

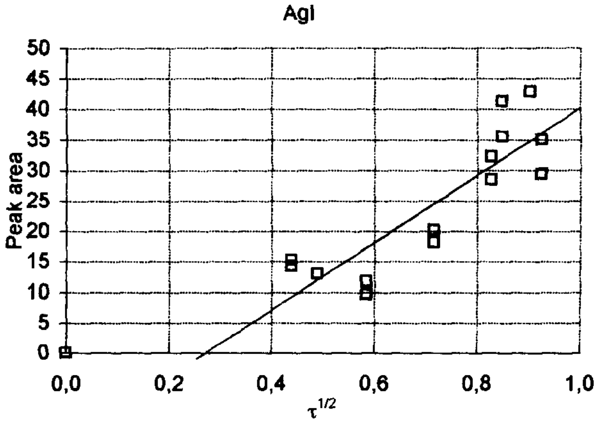

Fig. 2. Obtained areas of maximum peak intensity for AgI versus normalized exposure time to iodine.

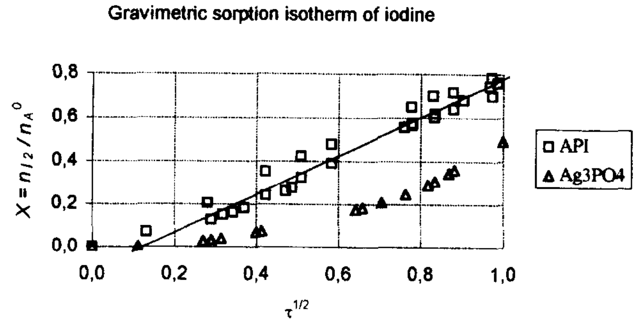

Fig. 3. Gravimetric sorption isotherms of iodine by API and Ag_3PO_4.

Table 1. Reflections of $\{Ag_3PO_4 + I_2\}$ obtained by the Debye–Scherrer method (Cu-K_α radiation). Exposure time: 2200 h. Reflections which are marked with • correspond to $\gamma - AgI$

d/Å	I	d/Å	I
3·72•	S	1·97	W
3·17	M	1·95•	S
2·81	W	1·86	W
2·34	M	1·62•	M
2·28•	VS	1·49•	M
2·23	M	1·41	VW
2·16	W	1·32•	M
2·09	W	1·25•	W
2·03	VW		

where K_i is a constant for a given peak of the substance i, C_i is the volumetric fraction of i and μ_m being the linear absorption coefficient of the sample given by $\mu_m = \sum C_i.\mu_i$, where μ_i is the linear absorption coefficient of the component substance of the sample.

Using eqn (4) with values corresponding to pure substance ($I_i = I_i^0$ and $C_i = 1$) we have

$$I_i^0 = \frac{K_i}{\mu_i} \tag{4}$$

and

$$C_i = \frac{I_i.\mu_m}{I_i^0.\mu_i} \tag{5}$$

The mole number (n_i) of API or AgI is

$$n_i = \frac{C_i.\rho_i.V_m}{M_i} \tag{6}$$

where ρ_i and M_i are the density and molecular mass of the '$_i$' component of the sample, V_m being the total volume of sample.

Substituting eqn (5) in eqn (6) we have

$$n_i = \frac{\rho_i.I_i.V_m.\mu_m}{I_i^0.M_i.\mu_i} \tag{7}$$

Carrying out the hypothesis that the iodine absorbed is in fact solid iodine

$$\mu_m = \frac{1}{V_m}.\left[\frac{M_A.\mu_A}{\rho_A}.n_A^0 + \frac{M_{I_2}.\mu_{I_2}}{\rho_{I_2}}.n_{I_2}\right] \tag{8}$$

Substituting eqn (8) in eqn (7) we obtain

$$\frac{n_i}{n_A^0} = \frac{\left(M_A.(\frac{\mu}{\rho})_A + M_{I_2}.(\frac{\mu}{\rho})_{I_2}.x\right)}{M_i.(\frac{\mu}{\rho})_i}.\frac{I_i}{I_i^0} \tag{9}$$

Expression (9) allows the mole number of API ($_i = _A$) and $\beta - AgI$ ($_i = \beta$) present to be known for $\tau \leq 1$.

On the other hand, if we express (9) for $_i = \beta$ and $\tau = 1$ ($x = y$ and $I_\beta = I_\beta^f$) we obtain

$$\frac{n_\beta^f}{n_A^0} = \frac{\left(M_A.(\frac{\mu}{\rho})_A + M_{I_2}.(\frac{\mu}{\rho})_{I_2}.y\right)}{M_\beta.(\frac{\mu}{\rho})_\beta}.\frac{I_\beta^f}{I_\beta^0} = \nu_\beta \tag{10}$$

where ν_β is the stoichiometric coefficient of AgI. Substituting we have $\nu_\beta = 3{\cdot}9 \pm 1{\cdot}2$. This value, within experimental error, would indicate that the stoichiometric equation for API decomposition in presence of gaseous iodine, for the first 200 h would be

$$\begin{aligned} Ag_7PO_4I_4(s) + yI_2(g) &\rightarrow 4\beta - AgI(s) \\ &+ \{Ag_3PO_4 + yI_2\}(s) \end{aligned}$$

where $y = 0{\cdot}78$. The value of ν_β obtained, with a measure of uncertainty arising from experimental error, is somewhat less than the stoichiometric coefficient of the reaction set down for a unitary degree of advancement of the same. Nevertheless a value higher than 4 would be expected, given that the hypothetical product of this reaction $\{Ag_3PO_4 + yI_2\}(s)$ (Table 1), should continue decomposing (Fig. 3), generating more AgI, seeing that it is the only X-ray detectable product of this reaction.

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