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Kinetics of the synthesis of ultradisperse cadmium and zinc oxide-like powders in a plasma-solution system

K V Smirnova, D A Shutov, V V Rybkin, A N Ivanov, M V Gromov

Ivanovo State University of Chemistry and Technology, Ivanovo, 153000 Russia

e-mail: shutov@isuct.ru

Abstract. The action of the DC glow discharge on the cadmium and zinc nitrates water solution in the absence of additional reagents and without electrodes-solution contact was shown to result in the production of the solids in the liquid phase. The atmospheric pressure direct current discharge was excited in the ambient air by applying a high direct voltage to two pointed titanium electrodes placed above liquid anode and liquid cathode in the H-shaped cell. The discharge current was varied in the range of 30-70 mA and the initional solutions concentrations were 5 mM. The kinetics of particles formation was studied using turbidimetry and nephelometry methods.

1. Introduction

In recent decades, interest in obtaining of nanomaterials has increased, which have unique mechanical, electrical, optical, magnetic and catalytic properties. Nanoparticles of metals, alloys, oxides, etc. have found wide application in microelectronics, powder metallurgy, in medicine for the precise delivery of medicines, as well as in the production of catalysts, dyes, lubricants and other fields.

There are many different methods for synthesizing micro / nano (ultradispersed) structures. Enough can be conditionally divided into three groups: first - the synthesis of nanoparticles in gaseous (vapor) phase; the second - mechanical synthesis (mechanosynthesis); the third is the synthesis of nanocharts in liquid (colloidal) systems. The latter include methods based on the action of gas discharges. In the last 10-15 years, a large number of works have appeared in the world, in which the possibilities of obtaining nanoparticles of metals, oxides and some other compounds using plasma-solution methods are shown. Various methods of excitation of discharges and plasma-chemical cells, used precisely for the purposes of synthesis, are considered in detail in the review papers [1, 2].

The most popular among researchers are nanoparticles of precious metals: Au, Pt, Ag, Pd. There are works devoted to the synthesis of Al, Ti, Fe, Co, Ni, Cu, Zn, Ge, Zr, Sn. From the composite materials, the structures of Au-Ag, Pt-Au, Ag-Pt, Co-Pt, Fe-Pt, Sm-Co, Ni-Cr, Sn-Ag, Sn-Pb, Co-B, Mo-S can be cited. Among the oxides synthesized with the help of plasma-solution systems, we can name oxides Al, Ti, Cu, Fe, Co, Zr, Ru, Sn, Ta, W, In and Zn. As far as we know there are no any papers devoted to plasma-solution synthesis of CdO. Also, there are no any data on the investigations of the kinetics of the solids formation in the liquid phase during solution treatment by discharge.

The main goal of this work was the investigation of the kinetics behaviors of the solid formation during atmospheric pressure direct current discharge treatment of the water solutions of the $Cd(NO_3)_2 \cdot 4H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$.

2. Experimental

Aqueous solutions of analytical grade $Cd(NO_3)_2 \cdot 4H_2O$ or $Zn(NO_3)_2 \cdot 6H_2O$ (JSC "Himreactiv", Russia) with a concentration of 0.005 mol/L, a volume of 200 ml, were placed in an H-shaped glass cell. The discharge was excited in the ambient air by applying a high direct voltage to two pointed titanium electrodes. So the solution surface of one of the cell is considered as liquid anode (A-cell) and of another cell as liquid cathode (C-cell). The electrode-solution surface distance was adjusted to 5 mm. The discharge current was varied in the range of 30-70 mA. The duration of solution treatment was 10 min. The experimental setup was described in detail in [3].

By the action of a discharge a colloidal solution was formed in the near-surface layer of A-cell and precipitate was formed at the bottom of the cell.

To characterize the kinetics of the particles formation process the turbidimetry and nephelometry methods were used. The intensity of light transmitted through the near-surface layer (1 mm below surface) of solution in first case, or the intensity of the scattered light in second case was measured using AvaSpec-2048FT-2 spectrometer (Avantes, Netherlands). Optical length was 45 mm in both cases. Scattering angle was 90°. The He-Ne laser (λ=632.8 nm) was used as a light source (Figure 1).
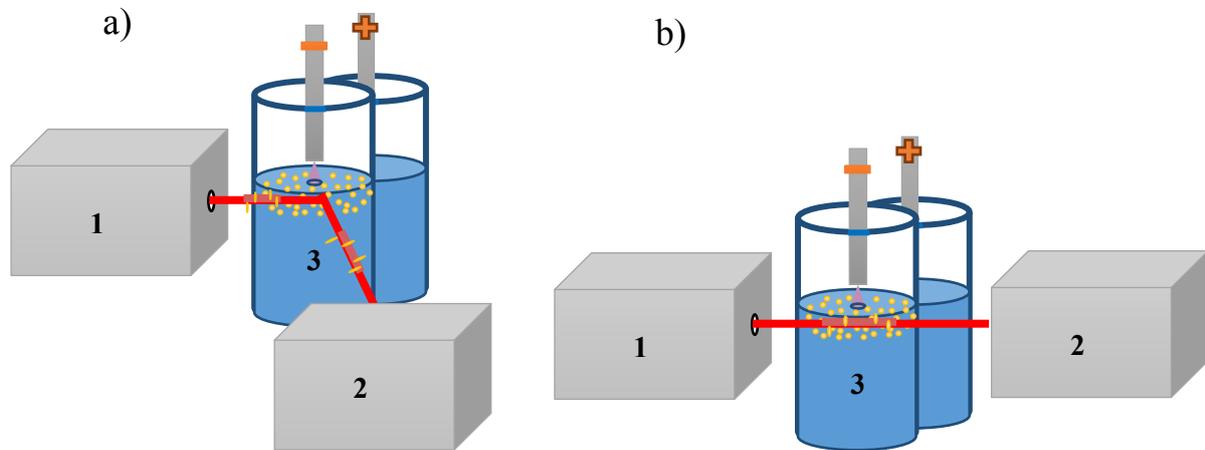

Figure 1. Schematic view of nephelometry (a) and turbidimetry (b) measurements: 1 – He-Ne laser, 2 – spectrometer, 3 – anodic cell.

3. Results and discussion

After the discharge ignition there are no any visible changes in both A-cell and C-cell at first tens seconds of solution treatment. Turbodimetry curve (Figure 2) demonstrates induction period of the process. After induction period a colloidal solution was formed in the near-surface layer of A-cell and precipitate formation started at the bottom of this cell. No colloid solution or precipitate was observed in the C-cell during treatment but a gas bubbles near the liquid phase surface always appeared.
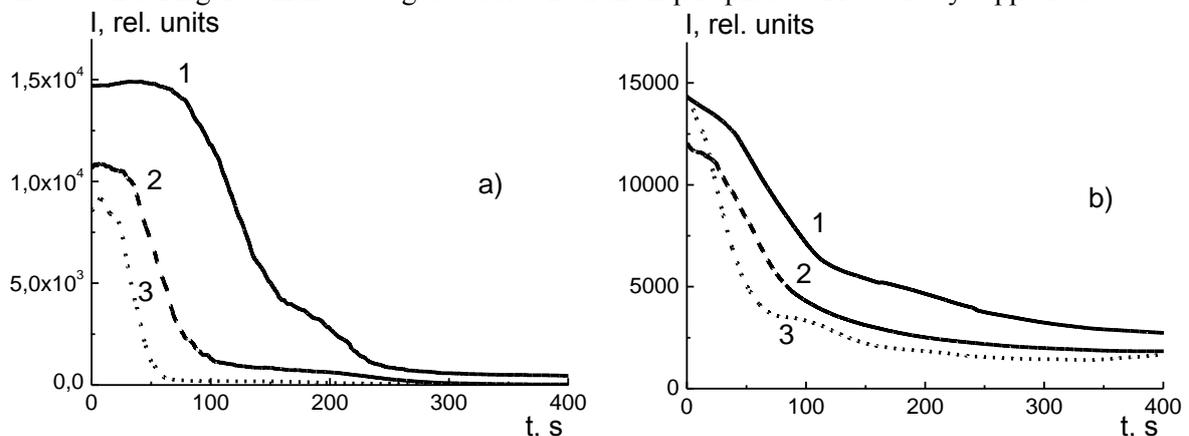
Figure 2. Turbidimetric kinetic curves of the $Zn(NO_3)_2 \cdot 6H_2O$ (a) and $Cd(NO_3)_2 \cdot 4H_2O$ (b) solutions: 1 – 30 mA, 2 – 60 mA, 3 – 70 mA.

The increase of the discharge current lead to the decrease of the induction period (figure 3a). At low input power the induction period of the Zn-containing powder formation is about two times higher than Cd-containing powder formation. But as discharge current increase the induction times becomes comparable.
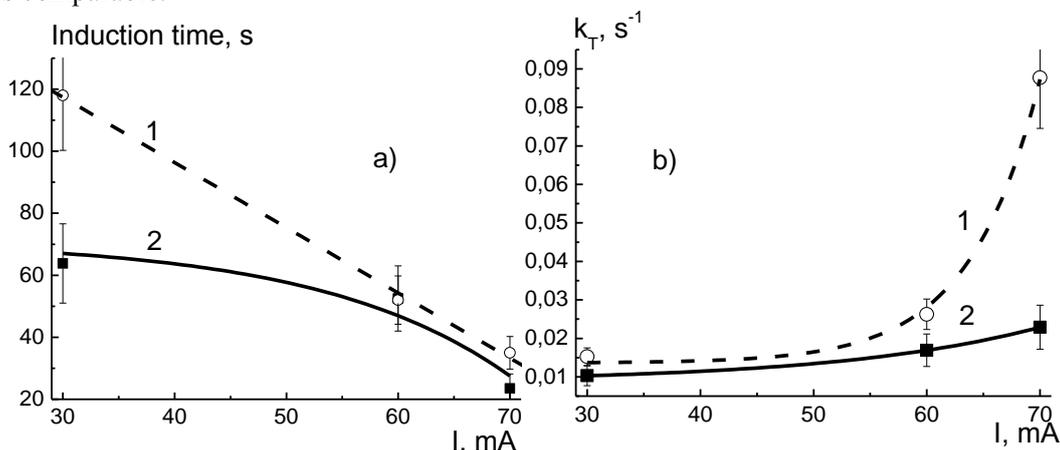

Figure 3. Induction period (a) and effective constant of the powder formation process (b): 1 – $Zn(NO_3)_2 \cdot 6H_2O$, 2 - $Cd(NO_3)_2 \cdot 4H_2O$

In turbidimetry the Beer's-low like expression for the intensity is applicable [4]:

$$I_T = I_0 e^{-\alpha_T C} \qquad (1),$$

where I_T – transmitted light intensity due to the scattering effect of particles suspended, I_0 - initial light intensity, α_T – coefficient of proportionality that included turbidity constant and light path length, and C – the concentration of scattering species.

In our case the concentration is a function of discharge treatment time, $C=C(t)$. But we don't exactly know the rate law for the particles formation process. The simplest assumption that kinetics of the species formation followed by zero-order law gives to us:

$$C = kC_0 t \qquad (2),$$

where k – effective solids formation rate constant, C_0 – initial concentration of nitrate. And the combination of (1) and (2) is:

$$I_T = I_0 e^{-\alpha_T k C_0 t} = I_0 e^{-K_T t} \qquad (3)$$

Really, the kinetics of the passed light intensity is described well with a formal first-order rate law (3) with an effective constant K_T of about 10^{-2} s^{-1} (pairwise correlation coefficient is 0.98) (figure 3b). It's should be noted that this coefficient characterizes not only solid species formation rate but includes flocculation and sedimentation processes. Also, we find out that the increase of the discharge current lead to the growth of the effective rate constant.

To check our assumption of zero-order law species formation (2) we have measured scattered light intensity during the discharge.

In the first approximation the intensity of scattered light is given by expression:

$$I_S = \alpha_S I_0 C \qquad (4),$$

where I_S –scattered light intensity, I_0 - initial light intensity, α_S – some empirical coefficient of proportionality, and C – the concentration of scattering species.

Theoretically combination of (2) and (4):

$$I_S = \alpha_S I_0 k C_0 t = I_0 K_S t \qquad (5)$$

gives the linear time's behavior of the scattered light intensity where the K_S is an effective constant. As it can be seen in figure 4a, nephelometry curve shows two near-to-linear parts. The curve consists of

four accentuated region (figure 4a). There is no noticeable increase in the scattering light intensity at initial time after discharge excitation (section I) and the induction period followed by the two sections of linear growth (sections II and III). It's should be noted that curve look's like typical topochemical kinetic curve where reactions are strongly localized, in our case in the area of the discharge-liquid contact point. After the growth sections the near-to-exponential decay of measured scattered light intensity is obtained (section IV). We assume that this interval deals with reabsorption and/or rescattering of the light in the high concentrated colloidal solution near the liquid surface.
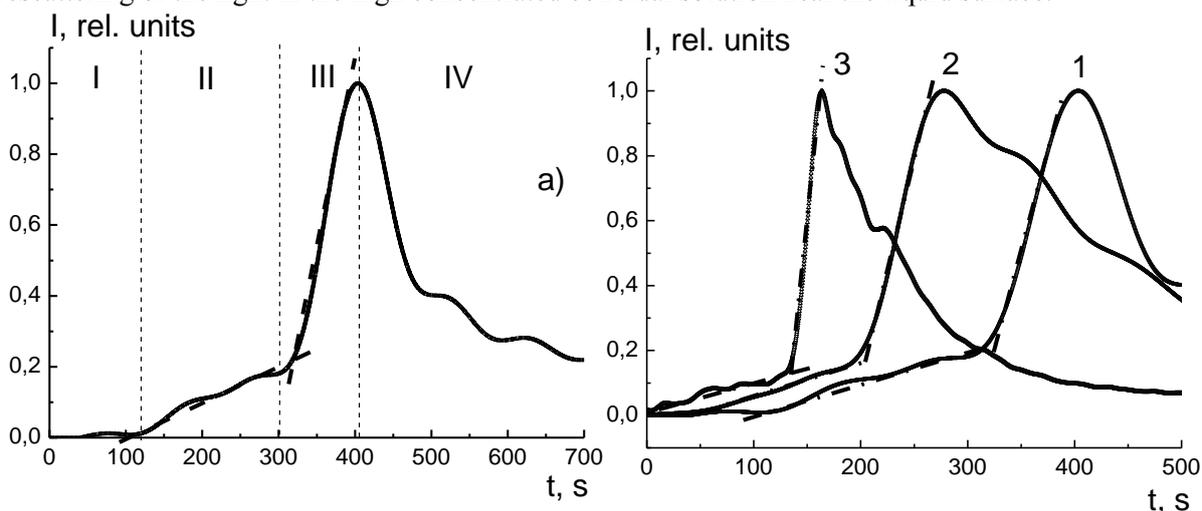

Figure 4. Different segments of nephelometry kinetic curves of the $Zn(NO_3)_2 \cdot 6H_2O$ at discharge current 30 mA (a) and nephelometry kinetic curves of the $Zn(NO_3)_2 \cdot 6H_2O$ (b) at currents of: 1 – 30 mA, 2 – 60 mA, 3 – 70 mA.

The calculated effective constants K_S are shown in table 1. The character of the constants changes with discharge current increase identical to the changes of K_T. Unfortunately, both K_S and K_T includes unknown coefficients α_S and α_T, respectively. So it is impossible to calculate effective solids formation rate constant k. Moreover, changes of the slop in nephelometry kinetic curves can be assigned with changes of the coefficient α_S, that is turbidity in fact.

Table 1. Effective constants K_S obtained from sections II and III of the figure 4b.

Discharge current (mA)	K_S^{II} (s^{-1})	K_S^{III} (s^{-1})
30	$0.94 \cdot 10^{-3}$	$1.22 \cdot 10^{-2}$
60	$1.08 \cdot 10^{-3}$	$1.46 \cdot 10^{-2}$
70	$1.3 \cdot 10^{-3}$	$3.48 \cdot 10^{-2}$

Anyway, the kinetics of the particle formation under the discharge action is complicated process and needs additional investigations.

4. Conclusion

The action of the glow discharge onto the water solution of $Cd(NO_3)_2 \cdot 4H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ lead to the formation of the powders in near-to-surface layer of the liquid anode. Increase of the discharge current lead to the increase of the powder formation rate. The powders formation kinetics in first approximation describes by the zero-order kinetics law.

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