2 Magnetic Impedance Method: The MHD Transfer Functions

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「磁気インピーダンス法と MHD 伝達関数を用いた反応解析」の解説

これは、電気化学反応における磁場効果としてよく知られている MHD (電磁流体力学) 効果の非定常応答を利用した、磁気インピーダンス法とその伝達関数についての論文である。著者の 1 人である Olivier 教授は、この方面の理論および実験における開発者であり、長年にわたって磁気電気化学の発展に貢献してきた方である。

この方法は、通常の電気化学系に磁場を加える場合に、同時に微小な変動磁場を重畳するところに、大きな特徴がある。その結果、電極界面に生じる溶液の運動 (MHD 流れ) に、周期的振動が加わることになる。そこでこの振動によって、電極系に誘起される電流もしくは電位の交流成分を計測し、反応解析を行うことができる。

従って、あらたな磁場効果の確認のほかに、通常の交流インピーダンス法と同様の測定が可能になる。さらに測定の結果、電極系に固有の MHD 伝達関数と呼ばれる特性関数が求まるが、この関数をいかにして求め、いかにして利用するかという点について、第一線で研究を進めている Devos 博士が中心になって、最近の成果をもとに、まとめられたものが本解説である。

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Abbreviations

A ; electrode surface	M ; modulus of the MHD transfer function	trode
B ; magnetic field	M_0 ; modulus of the MHD transfer function at low frequency range	x, y, z ; axis
C_i ; concentration of species i	V ; potential	α ; velocity gradient
C^* ; bulk concentration of electroactive species	d ; electrode diameter	δ ; thickness of the diffusion layer
D ; diffusion coefficient	j ; $\sqrt{-1}$	ϕ ; phase
F ; Faraday	k ; constant defined in equation (2)	γ ; experimental parameter defined in eq.(15)
f ; frequency	n ; electrons number involved in redox reaction	θ ; adsorbate surface ratio
$H(\sigma)$; transfer function	v_x ; flow velocity tangential to the electrode	σ ; dimensionless frequency
I ; current		ω ; pulsation
I_l ; limiting current		

1 Introduction

The aim of this paper is to extract the interest to use a new electrochemical analysis method using magnetic fields, namely, the MHD transfer function measurement. Indeed, the technique which consists of modulation of the magnetic field $\mathbf{B}$ around a mean value led to analyze electrochemical systems with complex mechanisms such as zinc or nickel electrodeposition and to provide new information about mechanisms occurring at the working electrode. Since many years, magnetic field $\mathbf{B}$ is used in electrochemistry as a forced convection tool like others more classical methods, *e.g.* rotating disc electrode.¹⁾ It is actually well established that a $\mathbf{B}$ applied in a parallel direction to the electrode surface generates a tangential convection near the working electrode when

an electrolytic current flows. This convection especially leads to an increase of the electrolytic current value when it is controlled by mass transport process.²⁻⁷⁾ Different theoretical approaches were performed in order to explain and quantify this phenomenon. In particular, the measurement of the limiting current value against $\mathbf{B}$ intensity led to establish different equations. For instance, R. Aogaki *et al.* expressed the limiting current proportional to $B^{1/2}$ or $B^{1/3}$ according to the type of the two electrode cell used.^{8,9)} T. Z. Fahidy proposed a statistical expression of the limiting current by using experimental results from various papers.¹⁰⁾ Macroscopic experimental and theoretical approaches about influence of $\mathbf{B}$ on mass transport phenomena were developed by O. Aaboubi *et al.* The stationary and

dynamical experimental results obtained with a classical three electrode cell confirmed theoretical expressions.^{11,12)} This work also led to introduce a new analysis dynamical technique, the MHD transfer function measurement. Recently, a new theoretical approach was developed by J. P. Chopart in order to investigate MHD effect at the electrode / electrolyte interface^{13,14)} which led to introduce a new experimental device for convective mass-transport analysis by electrokinetic-hydrodynamic effect.¹⁵⁾ Moreover, various studies consisted in investigation of the **B** influence on charge transfer kinetic¹⁶⁻¹⁸⁾ or structural and morphological changes of the electrodeposits,¹⁹⁻²²⁾ especially concerning the dendritic growth of metallic deposition under high magnetic field.²³⁻²⁵⁾ In this paper, we propose to emphasize the results obtained by using MHD transfer function measurements from zinc electrodeposition in basic media and nickel electrodeposition in Watts bath. The last part of this paper was devoted to show the results obtained by means of a new home-made apparatus less cumbersome than the usual one. At first, let us consider the theoretical approach of the MHD transfer function.

2 Theoretical Approach of the MHD Transfer Function

MHD transfer function measurement consists in measuring the frequency response of potential $|\Delta V| \sin(\omega t + \phi)$ or current $|\Delta I| \sin(\omega t + \phi)$ generated by a sinusoidal perturbation of the **B** around a mean value $B_0 + |\Delta B| \sin(\omega t)$.¹²⁾ This method completed others dynamical one, such as A. C. impedance or electrohydrodynamic, electro-gravimetric, opto-electric and thermo-electrochemical transfer function measurements.²⁶⁾ By using a frequency response analyzer, this method led to obtain two transfer functions $\Delta \tilde{I} / \Delta \tilde{B}$ in potentiostatic regime and $\Delta \tilde{V} / \Delta \tilde{B}$ in galvanostatic regime. The MHD transfer function measurement was presented for the first time by A. Olivier *et al.* in 1987.²⁷⁾ The sinusoidal modulation of the magnetic field ΔB generated a flow velocity modulation Δv_x which led to a concentration gradient perturbation of the electroactive species at the electrode surface $(d\Delta C / dy)_{y=0}$ which involved an electrolytic current modulation ΔI when this latter was controlled by mass transport as follow,

$$\Delta B \rightarrow \Delta v_x = \Delta \alpha y \rightarrow (d\Delta C / dy)_{y=0} \rightarrow \Delta I$$

v_x flow velocity tangential to the electrode surface
 α velocity gradient at the electrode surface defined by

$$\alpha = \left(\frac{\partial v_x}{\partial y} \right)_{y=0} \quad (1)$$

Experimental investigation led to write an expression of α as follow,^{11,12)}

$$\alpha = kBC^* \quad (2)$$

at the limiting current value. k represented an experimental constant obtained in steady-state, C^* was the bulk concentration of electroactive species.

Hence, the MHD transfer function could be written as a product of three transfer functions,

$$\frac{\Delta I}{\Delta B} = \frac{\Delta I}{(d\Delta C / dy)_{y=0}} \cdot \frac{(d\Delta C / dy)_{y=0}}{\Delta \alpha} \cdot \frac{\Delta \alpha}{\Delta B} \quad (3)$$

The first term of equation (3) was a real number if we considered a polarization point corresponding to the limiting current value such as,

$$\Delta I = nFAD(d\Delta C / dy)_{y=0} \quad (4)$$

The second term of equation (3) was obtained by resolution of non-steady state convective diffusion equation if the migration terms were neglected,

$$j\omega \Delta C + \alpha y \frac{\partial \Delta C}{\partial x} - D \frac{\partial^2 \Delta C}{\partial y^2} = -\Delta \alpha y \frac{\partial C}{\partial x} \quad (5)$$

Deslouis *et al.* wrote the expression of $(\partial \Delta C / \partial y)_{y=0}$ in the case of a rotating disc electrode with modulated velocity,²⁸⁾

$$\left(\frac{\partial \Delta C}{\partial y} \right)_{y=0} = C^* (\alpha D^2 d^5)^{1/3} \frac{\Delta \alpha}{\alpha} H(\sigma) \quad (6)$$

where $H(\sigma)$ was a transfer function and σ the non-dimensional frequency defined by

$$\sigma = \omega (d^2 / D\alpha^2)^{1/3} \quad (7)$$

The third term of equation (3) was considered to be a frequency independent real number in the experimental frequency range.

Therefore, MHD transfer function could be written from equations (3), (4) and (6) in the case of an unidirectional laminar flow tangential to a horizontal and circular microelectrode downward,^{11,29)}

$$\frac{\Delta I}{\Delta B} = nFC^* \left(\frac{D^2 d^5}{\alpha^2} \right)^{1/3} H(\sigma) \frac{\Delta \alpha}{\Delta B} \quad (8)$$

The numerical integration of $H(\sigma)$ led to write, For $\sigma \leq 6$

$$\left| \frac{H(\sigma)}{H(0)} \right| = (1 + 0.049\sigma^2 + 0.0006\sigma^4)^{-1/2} \quad (9)$$

$$\phi = -\arctg[0.242\sigma(1 + 0.012\sigma^2 - 0.00015\sigma^4)] \quad (10)$$

For $\sigma > 6$

$$\left| \frac{H(\sigma)}{H(0)} \right| = \frac{4.416}{j\sigma} - \frac{5.3}{(j\sigma)^{3/2}} \quad (11)$$

Fig. 1 Experimental current - voltage curves for $\text{Zn(OH)}_4^{2-} / \text{Zn}$ system in KOH 7 M plotted for various B . (a) $B=0$, (b) $B=0.3$ T, (c) $B=0.6$ T, $C_{\text{Zn(OH)}_4^{2-}}=0.2$ M, $C_{\text{KOH}}=7$ M, $v=20$ mV min^{-1} .

Fig. 2 Ratio of zinc electrodeposition limiting current I_l to Zn(OH)_4^{2-} concentration C^* vs. $(BC^*)^{1/3}$. (■) $C^*=0.1$ M, (◆) $C^*=0.15$ M, (▲) $C^*=0.2$ M, $C_{\text{KOH}}=7$ M, $d=5$ mm.

where $|H(\sigma)|$ and ϕ are respectively modulus and phase of the transfer function, and $H(0)=0.8075$.

MHD transfer function equations were experimentally validated by using a reversible electrochemical system, e.g. potassium ferri-ferrocyanide on platinum electrode.^{11,12,29}

3 Zinc Electrodeposition

In order to emphasize the influence of B on a typical electrochemical system mass transport limited, we proposed to study zinc electrodeposition from a basic media by means of stationary and dynamical analysis methods at the limiting current value I_l .³⁰⁻³²

3.1 Steady-state

From current - voltage curves, we could see that the limiting current of zinc electrodeposition is increased with B in agreement with previous studies (Fig. 1). Figure 2 represented I_l / C^* vs. $(BC^*)^{1/3}$ for a 5 mm diameter electrode. We could observe a straight line crossing the origin. This result was in perfect accordance with stationary theoretical expectations and with experimental data obtained from a reversible electrochemical system, $\text{K}_3\text{Fe(CN)}_6 / \text{K}_4\text{Fe(CN)}_6$ on platinum electrode.^{11,29} The theoretical expression of the limiting current value could be

Fig. 3 MHD transfer functions $(\partial I / \partial B)_v$ plotted in the Nyquist plane at zinc electrodeposition limiting current for various magnetic intensities B_0 . (●) $B_0=0.3$ T, (◇) $B_0=0.45$ T, (◆) $B_0=0.6$ T, (□) $B_0=0.75$ T, (■) $B_0=0.9$ T, $C_{\text{Zn(OH)}_4^{2-}}=0.2$ M, $C_{\text{KOH}}=7$ M, $d=5$ mm.

written,

$$I_l = 0.678 n F d^{5/3} D^{2/3} C^* (k B C^*)^{1/3} \quad (12)$$

Therefore, we could write the slope of the straight line,

$$s = 0.678 n F d^{5/3} D^{2/3} k^{1/3} \quad (13)$$

3.2 Dynamical investigation - MHD transfer function

The experimental MHD transfer functions $(\partial I / \partial B)_v$ were represented in the Nyquist plane for various magnetic field intensities B_0 (Fig. 3). Experimental device used to obtain these curves was described in previous papers.^{11,31} At the limiting current value, MHD transfer function measurements allowed us to isolate and characterize diffusion process of electroactive species, Zn(OH)_4^{2-} toward the working electrode. In agreement with the decrease of the thickness of the diffusion layer δ , the magnitude of the loop decreased as B intensity increased. The diagrams were represented in Bode plane for different Zn(OH)_4^{2-} concentrations and magnetic field intensities with modulus normalized (Fig. 4). From equations (2), (7) and (13), we could write,

$$\sigma = \omega (0.678 n F)^2 d^4 s^{-2} D (B C^*)^{-2/3} \quad (14)$$

The different experimental curves could be represented in single one according to $\log \sigma$. This result highlighted the hydrodynamic control of B on diffusing species Zn(OH)_4^{2-} in agreement with theoretical predictions. Moreover, Fig. 4 showed, for $\sigma \leq 6$, a good accordance between experimental data and theoretical expression of the MHD transfer function (8) for a diffusion coefficient value of Zn(OH)_4^{2-} , $D_{\text{Zn(OH)}_4^{2-}} = 5.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ in equation (14). This value was close to the coefficient value obtained from Levich's expression by means of rotating disc elec-

Fig. 4 Experimental and theoretical MHD transfer functions plotted in the Bode plane at zinc electrodeposition limiting current. $C_{\text{Zn}(\text{OH})_4^{2-}} = 0.1 \text{ M}$, ($\square$) $B_0 = 0.3 \text{ T}$, ($\diamond$) $B_0 = 0.6 \text{ T}$, ($\triangle$) $B_0 = 0.9 \text{ T}$, $C_{\text{Zn}(\text{OH})_4^{2-}} = 0.2 \text{ M}$, ($\blacksquare$) $B_0 = 0.3 \text{ T}$, ($\bullet$) $B_0 = 0.45 \text{ T}$, ($\blacklozenge$) $B_0 = 0.6 \text{ T}$, ($\blacktriangle$) $B_0 = 0.9 \text{ T}$, $C_{\text{KOH}} = 7 \text{ M}$. Solid line, theoretical diagram plotted from expression (8).

trode ($D_{\text{Zn}(\text{OH})_4^{2-}} = 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$).

From these results, we could conclude that hydrodynamic convection induced by **B** near the electrode surface perfectly controlled diffusion process of $\text{Zn}(\text{OH})_4^{2-}$ species for zinc electrodeposition from basic media. Theoretical expressions of MHD transfer function led to obtain the diffusion coefficient value of $\text{Zn}(\text{OH})_4^{2-}$ with a good accuracy at the limiting current value.

4 Nickel Electrodeposition

Nickel electrodeposition from a Watts solution is known to be an electrochemical system non limited by mass transport process. We proposed to investigate the **B** effect on such irreversible system by means of analysis electrochemical methods and structural investigation of the electrodeposits.^{22,32-34} In this part, we have only considered the results concerning the steady-state and MHD transfer function investigations.

4.1 From a Watts solution containing 2-butyne-1,4-diol (BD)

BD is an organic inhibitor limited by mass transport phenomenon added in small amount (usually 10^{-3} M) in the Watts bath. Experimental conditions were described in a previous paper.³³

4.1.1 Steady-state Figure 5 showed the

Fig. 5 ($\blacklozenge$) Electrocrystallization current vs. **B** intensity. Watts solution containing 10 mM 2-butyne-1,4-diol, $T = 30^\circ \text{C}$, $V = -0.93 \text{ V / SCE}$. Dashed line, current calculated from equation (15).

Fig. 6 MHD transfer functions $(\partial I / B)_v$ in Nyquist plane for Ni electrodeposition and various B_0 intensities. Same electrodeposition conditions as in Fig. 5, $d = 5 \text{ mm}$, ($\blacksquare$) $B_0 = 0.3 \text{ T}$, ($\square$) $B_0 = 0.45 \text{ T}$, ($\blacklozenge$) $B_0 = 0.6 \text{ T}$, ($\diamond$) $B_0 = 0.75 \text{ T}$, ($\blacktriangle$) $B_0 = 0.9 \text{ T}$.

electrodeposition current vs. **B** intensity. We could notice a strong decrease of the cathodic current as **B** increased. Indeed, MHD convection increased the diffusion flux of inhibiting species toward the electrode surface. Hence, higher concentration of BD induced a larger covering part of the active surface, thus hindering Ni electrodeposition.

4.1.2 Dynamical investigation - MHD transfer function

MHD transfer functions obtained for different values of B_0 were represented Fig. 6 in the same potential range as steady-state investigation. The diagram shape was the same as a previous work concerning electrochemical systems limited by mass transport, e.g. zinc electrodeposition from basic media (Fig. 3) or potassium ferri-ferrocyanide.^{11,12} From this dynamical result, we could characterize mass transport process of inhibiting species BD. In this present case, the real point defined in low frequency range had an opposite sign $(\partial I / \partial B)_v > 0$. From the real point value defined at low frequency range for different B_0 intensities, we have written the

Fig. 7 Schematic representation of the reaction mechanism which accounts for the cathodic current response to a **B**. Watts solution containing BD or pure Watts solution.

Fig. 8 Experimental current - voltage curves for nickel electrodeposition for various **B**. Pure Watts solution, $T=30^\circ\text{C}$, $\text{pH}=4.5$, (—) $B=0$, (Δ) $B=0.3\text{ T}$, ($\blacklozenge$) $B=0.6\text{ T}$.

expression of the stationary current as follow,³³⁾

$$I = I_{(v)} - 3\gamma B^{-1/3} \quad (15)$$

where $I_{(v)}$ was the I component independent of **B**, γ experimental parameter obtained through MHD transfer function measurements ($\gamma=0.25\text{ mA T}^{-1}$). Equation (15) was verified by the good accordance between steady-state investigation and calculated curve for magnetic fields higher than 0.18 T (Fig. 5).

This new expression showed that the cathodic current component influenced by magnetic field was inversely proportional to $B^{1/3}$, which led to represent this sequence,

$$\Delta B \rightarrow \Delta v_x \rightarrow \Delta(\partial C / \partial y)_{y=0} \rightarrow \Delta \theta \rightarrow \Delta I$$

The modulation of the MHD convection generated a perturbation of the convective flow at the electrode surface, which induced a modulation of the concentration gradient of BD. The catalyzed hydrogenation of the acetylenic alcohol led to an increase of the pH near the electrode / solution interface. This phe-

nomenon favored the precipitation of adsorbed hydroxyde such as $\text{Ni}(\text{OH})_2$ ³⁵⁾ and this latter hindered active surface for nickel electrodeposition. From EIS investigation, the change of the adsorption kinetic induced by the MHD convection was highlighted by the increase of the inductive loop magnitude in the low frequency range.³³⁾ Hence, the modulation of the cathodic current, observed through MHD transfer function measurements, came from the sinusoidal modulation of the adsorbate surface ratio θ (Fig. 7).

4.2 From a pure Watts solution

The kinetic of nickel electrodeposition from a Watts bath is not mass transport controlled. Nevertheless, different authors proposed to study this system with high speed rotating disc electrode ($>2000\text{ rpm}$) in order to eliminate any influence of convection and diffusion on the electrochemical results. We have investigated the MHD convection effect on such system.

4.2.1 Steady-state If we represented current - voltage curves from a pure Watts solution, for a potential range less cathodic than -910 mV / SCE , no variation of the electrolytic current value could be observed when **B** increased (Fig. 8). This result was in accordance with the kinetic control of the nickel electrocrystallization.

4.2.2 Dynamical investigation - MHD transfer function

Nevertheless, in a potential range less cathodic than -910 mV / SCE , the MHD transfer function measurements brought out same diagram shape as above in presence of BD but with a current modulation magnitude much weaker than in the above case (Fig. 9). The positive value of the MHD transfer function defined at low frequency range led to show the slight decrease of the cathodic current as **B** increased. From this result, the diffusion process of H^+ species toward the working electrode could be characterized. Indeed, cathodic current of nickel electrodeposition from a Watts solution included a component due to the reduction reaction of protons ions,³⁶⁾ and this secondary reaction was mass transport controlled.³⁷⁾ Hence, we proposed the same mechanism as previously when adding a small amount of BD (Fig. 7). The proton diffusion was controlled by MHD convection. The reduction reaction led to a weak increase of the catholyte pH value which favored hydroxyde formation at the electrode surface. This phenomenon involved a weak decrease of the cathodic current because of the covering of the electrode area by inhibiting species such as adsorbed nickel hydroxyde. By using the real point at low frequency range $(\partial I / \partial B)_{\omega \rightarrow 0}$ for different values of B_0 , we could write the same stationary expression (15) obtained from a Watts solu-

Fig. 9 MHD transfer functions $(\partial I / \partial B)_v$ in Nyquist plane for Ni electrodeposition and various B_0 intensities. Pure Watts solution, $T=30^\circ\text{C}$, $\text{pH}=4.5$, $V=-0.88\text{ V / SCE}$, $d=5\text{ mm}$. (■) $B_0=0.3\text{ T}$, (□) $B_0=0.45\text{ T}$, (◆) $B_0=0.6\text{ T}$, (◇) $B_0=0.75\text{ T}$.

Fig. 10 Schematic representation of the experimental device for MHD transfer function measurement by using permanent magnets.

tion with BD. In this case, the very weak value of γ ($\gamma=25\text{ }\mu\text{A.T}^{-1}$) due to the small H^+ concentration in Watts solution ($\text{pH}=4.5$), did not permit to distinguish any variation on the electrolytic current from stationary I-V curves (Fig. 8).

5 New Experimental Device for MHD Transfer Function Measurements

This part is devoted to the presentation of the improvement of the technique permitting the MHD transfer function measurement. This new experimental device used small permanent magnets (2 cm in diameter) to apply a magnetic field near the electrode surface in vertical position (Fig. 10).²⁹ Previously, the magnetic field was applied to the whole experimental cell by using an electro-magnet with pole

Fig. 11 MHD transfer function $(\partial I / \partial B)_v$ plotted in the Nyquist plane for $0.15\text{ M K}_3\text{Fe(CN)}_6$ and $\text{K}_4\text{Fe(CN)}_6$ in 1 M KCl at the limiting anodic (■) $B=303\text{ mT}$ and cathodic, (◆) $B=136\text{ mT}$ currents, $d=2\text{ mm}$.

pieces 20 cm in diameter.^{11,12,31} The $\mathbf{B}$ modulation induced by this new apparatus was generated by the rotation of a disc which carried four permanent magnets as described Fig.10. The rotation speed of the plate determined the frequency of the $\mathbf{B}$ modulation. Experimental MHD transfer functions obtained by means of this device were presented Fig. 11. The used electrochemical system was oxydo-reduction of potassium ferri-ferrocyanide in 1 M potassium chloride on platinum disc electrode. Experimental diagrams were in perfect agreement with theoretical expectations and experimental data obtained previously by using electro-magnet. Moreover, this device emphasized some advantages in comparison to the previous one, higher modulation frequency, lower induced Lenz electromotive force and better accuracy on the measurement.

6 Conclusion

Dynamical investigations from MHD transfer function measurements led to show that all the modifications generated by $\mathbf{B}$ were due to the increase of diffusion flux through MHD convection. Indeed, by using this experimental technique, which consisted of modulation of $\mathbf{B}$, the mass transport process can be characterized and isolated in particular from a complex mechanism including different elementary steps. Notably in the case of nickel electrodeposition, the both effects of $\mathbf{B}$ on adsorption process observed from EIS investigation³³) as well as on morphology and texture changes of electrodeposits²²) come from the influence of the MHD convection on inhibiting species such as BD or H^+ from a pure Watts solution. This dynamical method leads to establish the stationary current influenced by $\mathbf{B}$ is inversely proportional to the diffusion flux of inhibiting species even in very

small concentration. Moreover, for zinc electrodeposition from basic media, the good agreement between experimental results and theoretical equations of the MHD transfer function allowed us to determine with a good accuracy the diffusion coefficient of $\text{Zn}(\text{OH})_4^{2-}$. Finally, the improvement of the experimental device for MHD transfer function measurement, by using small permanent magnets near the electrode surface, allowed us to increase the accuracy of experimental results and notably to increase the high frequency range. So this MHD technique will allow new investigations on many multisteps electrochemical reactions.

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3 磁気電気化学における非線形現象

茂木 巖

1 はじめに

強磁場が身近なものになってきた。液体ヘリウムを必要としない超伝導マグネットが開発されたからである¹⁾。様々な分野の実験が強磁場中で行われるようになり、「強磁場科学」とでも呼ぶべき学際的な学問領域が広がりつつある^{2,3)}。従来電気化学の分野においては、電磁石または永久磁石を用いて1 T以下の磁場中で磁気流体力学的(MHD)効果の研究が行われてきた^{4,5)}。最近になって5~10 Tの磁場を印加することによりはじめて顕在化するマイクロMHD効果などが見つか⁶⁻⁸⁾。材料開発への応用などの期待とも相まって磁気電気化学も活況を呈してきた。他方、より複雑な系への磁場の影響を研究する動きもある。電析過程で形成されるフラクタルパターン形成や電流の自励発振のような非線形現象への磁場効果の研究である。殊に磁気電気化学と形の科学の接点には思いの外、創造性豊かな世界が広がっていた。ここではそのような研究の一端を紹介したい。

2 形の科学と電気化学

1980年頃から統計物理学の分野で、自然界における無秩序な形を学問的に取り扱おうとする気運が高まってきた。マンデルブロがフラクタルの概念を導入し⁹⁾、ウィッテンとサンダーがフラクタルな形態形成のモデルとして拡散律速凝集(Diffusion Limited Aggregationの頭文字からDLAと呼ばれる)¹⁰⁾を提唱したのが契機となった。拡散に支配された凝集過程はラプラス方程式 $\nabla^2 C = 0$ (C は濃度)により記述されるが、成長界面の不安定性のため方程式は非線形

となり、界面の運動を記述する解を求めることはできない。DLAモデルはランダムウォークする粒子を種粒子の周りに凝集させるという極めて単純なシミュレーションを行うことにより、不規則に枝分かれしたフラクタルパターンを再現できることを示した。DLAはそのプロセスの単純さと、得られるフラクタル次元の普遍性から、自然界の多くのフラクタルパターン形成のモデルとしても盛んに研究されるようになった。そこで今度は実験室レベルでDLAを実現できる系の探索が始まった。そのモデル実験として最初に選ばれたのが2次元的空间内での亜鉛の電析成長、いわゆる金属葉である¹¹⁾。

硫酸亜鉛水溶液に電極を入れ電気分解すると陰極の周りに亜鉛が析出する。これを2枚のガラス板の間で行うか、あるいは油と水の界面を利用することにより2次元的に成長させることができる。その析出形態はたしかにDLAパターンを示し、フラクタル次元も1.66と求められた¹¹⁾。ところが電析形態には印加電圧や金属イオン濃度、他の要因により様々なパターンが現れる^{12,13)}。さらにそれらのパターンの幾つかは、電析に限らず他の系においても共通に観察される。そこで、そのようなパターン形成がどのようなメカニズムで起こるのかという新たな興味が生まれた。

3 強磁場に咲く銀の華

さて筆者らの行った実験を紹介しよう。磁場中を運動するイオンはローレンツ力の作用を受け回転運動を行う。ランダムウォークしながら拡散する粒子にローレンツ力が作用したとき、凝集パターンはどのように変化するであろうか。その