



OPEN Chaos-enhanced manganese electrolysis: nodule suppression and improved efficiency using controllable chaotic electrical signals

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The control and industrial application of chaotic systems is a major obstacle limiting the diffusion of chaos theory. In this study, we proposed a novel, universally applicable methodology for constructing an offset boosting function for chaotic systems. By integrating this approach with traditional techniques, a four-dimensional chaotic system with two-dimensional offset boosting was developed and successfully implemented by a real chaotic circuit for manganese metal electrolysis, replacing conventional DC. It has been shown that the use of time-varying electricity facilitates the suppression of electrochemical oscillations, and inhibits the growth of spherical manganese nodules. An examination of current efficiency for different oscillations (period 1, period 2, chaos-a and chaos-b) and various current amplitudes has established that chaos-a electrical signals are most suitable for inhibiting the growth of manganese nodules. The Mn nodule area ratios can be reduced by 38% with a 5.83% increase in current efficiency, representing an energy consumption saving of 0.58 kWh/kg. This interdisciplinary approach holds promise for advancing the study of nonlinear dynamic behavior in electrochemical reaction processes and addressing critical challenges in various fields, such as energy dissipation, quality improvement of electrodeposited products, and regulation of by-product properties.

Keywords Chaotic system, System control, Chaotic-circuit application, Electrodeposition, Manganese, Current efficiency

Background and significance

Electrodeposition, as a widely applied technique for metal fabrication, plays a crucial role in industrial production and fundamental scientific research^{1,2}. However, conventional direct current (DC) electroplating methods can suffer from low efficiency, high energy consumption, and difficulty in terms of precision in controlling the morphology of the deposited products^{3,4}. Improving the current efficiency in high-energy-consuming industries is a pressing issue as the cost of electrical energy is a major component of product costs, representing a critical requirement for sustainable development⁵.

This study considers the design and implementation of a novel chaotic circuit with controllability features that include amplitude control, multi-waveform output, and two-dimensional offset boosting, to meet complex engineering requirements. The developed chaotic circuit is applied to a manganese metal electrolysis system, replacing traditional DC sources, in order to explore the possibility of suppressing electrochemical oscillations and controlling the growth of manganese nodules. The work undertaken has provided the first experimental evidence of the benefit of chaotic currents relative to conventional DC and other forms of currents (such as

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periodic currents) in enhancing current efficiency, reducing energy consumption, and improving product quality.

This study establishes the unique benefits of chaotic currents in electroplating, providing empirical support for application in complex electrochemical systems^{6–8}. An improvement in electroplating efficiency with lower energy consumption is critical on an industrial scale, opening new avenues for sustainable development in high-energy-consuming industries, enabling energy conservation with associated economic benefits. This work advances the development of natural sciences and supports technological progress with energy conservation in high-energy-consuming industries.

Literature review

Systems change over time, notably those in engineering, physics, chemistry, biology, electromagnetism, and those associated with atmospheric and geological phenomena, which has led to the concept of dynamic systems⁹. There is a significant number of nonlinear motions in nature, which are described by nonlinear equations including ordinary differential, partial differential, and algebraic equations^{10,11}. The chaotic state represents a special case in nonlinear systems because of its complexity and infinite periodic characteristics. Chaos theory may be considered an evolutionary theory between orderly and disorderly state systems. An exploration of chaos requires an analysis of irregular and unpredictable phenomena and processes^{12,13}. Chaos theory, relativity and quantum mechanics are recognized as the greatest discoveries in the 20th century and masterpieces of the scientific community^{14,15}.

Chaotic systems represent a distinctive class of nonlinear systems with initial value-sensitive dynamics, where a minor alteration may have a considerable impact on the dynamic behavior^{16,17}. Consequently, the capacity to exert stable control over chaotic systems represents a pivotal advancement in expanding the possible applications of chaotic circuits. The most prevalent control methods include amplitude control and offset boosting, which are employed in the context of discrete^{18–20} and continuous chaotic systems^{21,22}. A system with two simultaneous bias directions is termed a two-dimensional offset boosting²³, and a chaotic system with both amplitude and offset controllability is designated a completely controllable system²⁴. Leutcho G. D. et al.^{25–27} have conducted extensive research on amplitude control, offset boosting, and the multistable evolution of chaotic systems.

Manganese is regarded as a strategic metal element, commonly employed as a fundamental ingredient for the fabrication of diverse alloys and novel energy materials^{28–31}. The process of metal preparation by electrodeposition necessitates a significant consumption of electricity which is an important cost factor for electrolysis processes³². An improvement in current efficiency (CE) and reduction of energy consumption (EC) are essential commercial considerations³³. Current efficiency is an important factor in energy consumption that is influenced by a range of factors. Chen³⁴ employed a slurry electrolysis system to treat reclaimed copper smelting fly ash with a CE of 91.22%, enabling an effective recovery of copper. At an extended electrolysis time, the pH in both the anode and cathode regions decreases, with a more significant drop at the anode. Xu³⁵ has reported an aluminum extraction from AlCl_3 -NaCl molten salts resulting in a deposited aluminum coating with a purity of 99.7%, and a CE of 44–64%. The decrease in CE was mainly related to the formation of dendritic or powdery aluminum deposits that readily entered the electrolyte.

Product quality and production capacity are essential factors in commercial manganese metal electrodeposition processes. Optimizing production capacity while guaranteeing product quality is challenging. Manganese electrodeposition is a non-equilibrium kinetic process, where temporal, spatial and energetic variations are complex^{36,37}. Electric energy serves as the primary source of energy input for the electrodeposition process, and the primary driving force for the spatially oriented deposition of manganese nodules. Therefore, it is theoretically feasible to modulate the kinetic behavior of manganese metal through variations in the input characteristics of the current waveform, with the potential to extend this technique to a broader range of electrochemical applications.

We have recently completed three phases of research on the chaotic current (CC) electrodeposition of manganese metal. In the first stage, the design and associated problems with CC electrodeposition equipment were overcome, and the electrodeposition of manganese metal was successfully realized with self-designed chaotic circuits and power amplifiers. Three issues were identified in the initial iteration of chaotic electrolysis. The first issue relates to the narrow CC fluctuation range, which complicates a differentiation from DC electrolysis. The second issue pertains to the self-designed current amplifier module, which exhibits a heating problem with a consequent loss of output stability. The third issue is associated with the difficulty in effectively suppressing electrochemical oscillations³⁸.

In the second phase of the research, a novel chaotic circuit with a broader voltage range was designed to address the limitation of the narrow fluctuation CC range. To overcome the problem of unstable operation, a commercial power amplifier was utilized to achieve a stable and continuous output of chaotic electrical signals. The results have demonstrated a complete suppression of electrochemical oscillation for the first time. To overcome the difficulty of quantifying Mn nodules, a semi-quantitative calculation of the nodule distribution area was achieved using a self-designed image processing technique. It has been demonstrated that a significant number of manganese nodules are formed when the current density is excessively high³⁹. The growth of manganese nodules results in the dissipation of energy, a reduction in product quality, a decline in current efficiency, and an increase in energy consumption. The inhibition of Mn nodule growth at higher current represents a pivotal factor in enhancing production capacity. However, the extent of the CC remains unregulated.

The third stage focused on the effect of current fluctuation range on Mn electrodeposition. A chaotic circuit with complete control (amplitude control and offset boosting) was designed and systematically investigated. It was demonstrated that a CC with a larger fluctuation range contributes to improved electrodeposition CE⁴⁰. Nevertheless, the drawback associated with effect of the current waveform and electrodeposition time has not been investigated.

Innovation and contributions

Building on the findings of the preceding research, four new studies are presented in this paper. A comparison with reported literature and previous work is shown in Table 1:

The principal contributions of these studies are as follows:

- 1. To satisfy complex engineering requirements, a new chaotic circuit with two-dimensional offset boosting has been devised to enhance the adaptability of chaotic power. The current can be regulated by the offset boosting voltage dimension, which streamlines the configuration of chaotic power. In addition, this study reports for the first time the use of offset boosting technology to achieve control over the current magnitude, replacing the conventional series resistor voltage divider module and optimizing the chaotic power supply electrolysis apparatus.
- 2. For the first time, this study investigates the impact of different waveform currents on the electrodeposition behavior of metallic manganese. The significant influence of the electrical signal waveform on the current fluctuation range of the current is established, demonstrating the superiority of CC over DC and periodic-state currents.
- 3. The effect of CC electrolysis time on the growth of manganese nodules is investigated for the first time. The gradual growth of spherical nodules was monitored using microscopy. It was found that Mn nodule growth can be significantly inhibited by CC at varying electrolysis times. In addition, the appreciable impact of electrolysis time on the electrolysis CE has been established. It is proposed that the effective inhibition of manganese nodule growth and improved CE can be achieved by altering the initial interfacial electrochemical reactions through CC.
- 4. It is proposed that the inhibition of manganese nodules can improve product quality, which is supported by X-ray photoelectron spectroscopy (XPS) analysis showing differences in the valence and elemental distributions of metallic manganese products with varying nodule content. This suggests that CC has the potential to improve the quality of manganese products by effectively inhibiting nodule growth.

Methods

Reagents and materials

The experimental setup involved one cathode and one anode. The cathode consisted of a single rectangular plate of stainless-steel type 304 having an area ($S = 2\text{ cm} \times 2\text{ cm} \times 1\text{ sides}$) of 4 cm^2 and a thickness of 0.5 mm . The anode consisted of plates of a lead-based quaternary alloy ($\text{PbSn}_{0.4}\text{Ag}_{0.014}\text{Sb}_{0.014}$) with a total area ($S = 2\text{ cm} \times 2\text{ cm} \times 2\text{ sides}$) of 8 cm^2 , and an approximate thickness of 3 mm . The electrolytic cell, formed from an acrylic sheet had an internal length of 11.5 cm , width of 3.6 cm , and height of 6.2 cm . The distance between the cathode and anode was 5 cm . A nonwoven fabric layer separated the cathode and anode to ensure a stable pH. Purified water was prepared using a water purification system (HMC – WS10, Human Company, South Korea). The manganese sulfate electrolyte was composed of 92 g/L MnSO_4 , $120\text{ g/L (NH}_4)_2\text{SO}_4$ and 30 mg/L SeO_2 (analytical pure reagents). Aqueous ammonia was used to adjust the pH to 7, and simulate electrolysis in industrial manganese electrodeposition applications. As temperature influences ion hydrolysis, and affects pH, the solution was heated to 40°C before adjusting the pH to 7.

Electrochemical device

Electrochemical experiments were performed using a two – electrode electrochemical workstation (CHI660E, Shanghai ChenHua Co., China). The distance between the anode, cathode and reference electrode was $2 \pm 0.02\text{ cm}$. A square cathode was used in the electrochemical oscillation tests, with a thickness of 1 mm and an area of 1 cm^2 ; the anode was cone – shaped and immersed in the solution.

Source	Coexisting attractors	Amplitude control	Offset boosting	Hardware	Application domain
Zhang et al. ⁴¹	No	Yes	Three-dimensional offset boosting	Yes	No
Chen et al. ⁴²	Yes	No	Initial-offset boosting	Yes	Neuron model
Li et al. ⁴³	Yes	Yes	No	Yes	Review article
Jiri Petrzela ⁴⁴	Yes	No	No	Yes	Lumped chaotic systems
Qiu et al. ⁴⁵	Yes	No	No	Yes	Secure communication
Xie et al. ⁴⁶	No	No	No	Yes	Reduced amplitude of electrochemical oscillations.
Yang et al. ³⁸	Yes	No	No	Yes	
Yang et al. ³⁹	No	No	No	Yes	First complete suppression of electrochemical oscillations.
Yang et al. ⁴⁰	Yes	Yes	No	Yes	A systematic study of the effect of current fluctuation amplitude on Mn metal electrodeposition.
This work	Yes	Yes	Yes	Yes	The effect of waveform and time on the current efficiency of Mn metal was studied for the first time.

Table 1. Chaotic system reported in previous literature.

Characterization methods

The phase composition was analyzed by the X-ray diffraction (XRD, PANalytical X'Pert Powder, Panalytical B.V., Netherlands). The microstructure was determined using scanning electron microscopy (SEM, JSM-7800 F, JEOL, Japan). Analysis of the chemical composition and structure of the electrodeposition products employed X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, Thermo Fisher Scientific, USA), Raman spectroscopy (RS, LabRAM HR Evolution, HORIBA Jobin Yvon S.A.S., France), and transmission electron microscopy (TEM, Talos F200S, Thermo Scientific, USA).

Data processing

Equations (1) and (2) were used to calculate current efficiency and energy consumption, respectively⁴⁷.

$$\eta_c = \frac{\Delta M_c}{E_{Mn} I_c \Delta t} \quad (1)$$

$$W_{Mn} = \frac{V \times 1000}{E_{Mn} \times \eta_c} \quad (2)$$

where η_c represents the cathodic current efficiency expressed as a percentage, $\Delta M_c/\Delta t$ (g/s) is the weight gain of the cathode at the time interval Δt , I_c denotes current (A), and E_{Mn} is the electrochemical equivalent, which is equal to 1.025 g/A·h for Mn. The W_{Mn} parameter represents the unit energy consumption of Mn (kW·h/t), and V is the cell voltage (V). To minimize experimental error, the average current and voltage during the entire electrodeposition process are reported in this paper, based on data collected by the current and voltage analyzer.

The path from theory to application

Method for constructing offset boosting function for any-chaotic system

A variety of tunable multi-channel chaotic signal sources are required to accommodate increasingly complex systems and meet engineering requirements. The variable-boostable (VB) chaotic system, designated as VB11 (Eq. 3)⁴⁸, featured only one-dimensional offset boosting. Therefore, the incorporation of a two-dimensional offset boosting can enable the output of more chaotic signals, thereby meeting diverse industrial requirements.

A new one-dimensional variable w is introduced into the original chaotic system to achieve offset boosting. The format is as follows:

$$\frac{dw}{dt} = cz - dw + d_2 \quad (3)$$

where c , d , and d_2 are arbitrary constants.

To further validate the universal applicability of this method, the Lorenz system and the Chen system were chosen as examples to undergo coupling computations with offset functionality (Table 2). It was observed that the attractor projection structures of the original chaotic systems on the x - z plane remained virtually unaltered after the coupling, confirming that the dynamics of the original chaotic systems were not perturbed by this method (Fig. 1a-f). Therefore, the signal characteristics of the original systems can be well-preserved.

Adjustments to parameters c and d enabled the scaling of signals in the w -dimension of the chaotic system (Fig. 1g-l) and resulted in attractor shifts in both the Lorenz and Chen systems. Moreover, the parameter d_2 has been successfully employed to achieve arbitrary offsets in the w -dimension for all three systems, which demonstrated the feasibility and universality of this method (Fig. 1m-o). After transformation, the system VB 11 can achieve simultaneous offset boosting in the x and w dimensions.

Dynamic properties of the chaotic system

The Lyapunov exponent is a key indicator of whether a dynamical system is chaotic or not. A positive Lyapunov exponent indicates that the system is in a chaotic state. The Lyapunov exponent of system (5) is $LE_1 = 0.06950$, $LE_2 = 0.0000$, $LE_3 = -0.4674$, $LE_4 = -10.0000$ when $a = 1$, $b = 2.75$, $c = 12$, $d = 10$, and $d_2 = 0$ the system is chaotic.

According to the chaos theory, a high value of Kaplan-Yorke dimension directly corresponds to high complexity of system dynamics⁵¹. The corresponding Kaplan-Yorke dimension for the suggested system (5) is computed as follows:

$$D_L = 3 + \frac{LE_1 + LE_2 + LE_3}{|LE_4|} = 3.05369 \quad (10)$$

The fractional nature of the Kaplan-Yorke dimension is seen from Eq. (5). Thus, the attractor is chaotic because of the fractional Lyapunov dimension⁵². For clear plots of attractors and Lyapunov exponents, the transient process is ignored, where the initial 100,000 points are neglected.

To gain further insight into the dynamic behavior of the system with parameter variation, bifurcation diagrams and Lyapunov exponents (Fig. 2a) were calculated. These demonstrate that system (5) exhibits clear dynamic behavior, which includes the state of period 1 (Fig. 2b), period 2 (Fig. 2c), chaos-b (Fig. 2d), and chaos-a (Fig. 2e). Moreover, the system also exhibits coexisting attractors that illustrate the initial value sensitivity of a

Chaotic system	Primitive 3D-chaotic system	Reconstructed 4D-chaotic system
VB11 chaotic system ⁴⁸	$\begin{cases} \frac{dx}{dt} = y+z \\ \frac{dy}{dt} = y^2 - az \\ \frac{dz}{dt} = x + by \end{cases} \quad (4)$ where $a=1, b=2.7$.	$\begin{cases} \frac{dx}{dt} = y+z \\ \frac{dy}{dt} = y^2 - az \\ \frac{dz}{dt} = x + by \\ \frac{dw}{dt} = cz - dw + d_2 \end{cases} \quad (5)$
Lorenz chaotic system ⁴⁹	$\begin{cases} \frac{dx}{dt} = \delta(y - x) \\ \frac{dy}{dt} = \gamma x - y - xz \\ \frac{dz}{dt} = xy - \eta z \end{cases} \quad (6)$ where $\delta=10, \eta=8/3, \gamma=28$.	$\begin{cases} \frac{dx}{dt} = \delta(y - x) \\ \frac{dy}{dt} = \gamma x - y - xz \\ \frac{dz}{dt} = xy - \eta z \\ \frac{dw}{dt} = cz - dw + d_2 \end{cases} \quad (7)$
Chen chaotic system ⁵⁰	$\begin{cases} \frac{dx}{dt} = A(y - x) \\ \frac{dy}{dt} = (C - A)x - xz + cy \\ \frac{dz}{dt} = xy - Bz \end{cases} \quad (8)$ where $A=35, B=3, C=28$.	$\begin{cases} \frac{dx}{dt} = A(y - x) \\ \frac{dy}{dt} = (C - A)x - xz + cy \\ \frac{dz}{dt} = xy - Bz \\ \frac{dw}{dt} = cz - dw + d_2 \end{cases} \quad (9)$
where c, d and d_2 are constant terms for the system parameters.		

Table 2. Chaos system equations and their corresponding parameters.

chaotic system. The coexisting attractors and corresponding attraction basin are presented in Fig. 2f-k. The waveform characteristics of different dimensional signals and corresponding frequency spectrum characteristics (Fig. S1a, b), and chaotic attractor structures in various planes when the system is in a chaotic state are illustrated in Fig. S1c-f.

System (5) has a special structure where the introduction of two new constants does not disturb the other dimensions, providing the condition for offset boosting. To clearly show this mechanism, a constant d_1 was added to the variable x and a constant d_2 was added to the variable w :

$$\begin{cases} \frac{dx}{dt} = y+z \\ \frac{dy}{dt} = y^2 - az \\ \frac{dz}{dt} = x + d_1 + by \\ \frac{dw}{dt} = cz - d(w + d_2) \end{cases} \quad (11)$$

where $a=0.9, b=2.9, c=12, d=10$, and the initial value was (0.4 0 0.1 0).

The chaotic attractor of system (11) can be controlled by the constant d_1 located at various positions in the direction of x , where the values in the other dimensions are not changed. The positions of the attractor in the direction of w can also be controlled by the constant d_2 according to the same principle. The chaotic attractor of system (12) can be controlled by the constant d_1 locating at various positions in the direction of x (Fig. S2a), and the values in the other dimensions are not changed (Fig. S2b). The positions of the attractor in the direction of w can also be controlled by the constant d_2 (Fig. S2e), and the values in the other dimensions are not changed (Fig. S2f). The transformation does not result in a variation of the dynamic behavior of the chaotic system, which has been proven by results of the Lyapunov exponents (Fig. S2d, h) and the bifurcation diagram (Fig. S2c, g). Accordingly, the proposed two-dimensional offset boosting in both the x and w directions is established (Fig. 2l).

Considering the linear terms and nonlinear terms in system (11), special nonlinearity offers the merit of complete amplitude control, including amplitude rescaling and easy offset boosting. Where $x \rightarrow mx, y \rightarrow my, z \rightarrow mz, w \rightarrow mw, t \rightarrow t (k > 0)$, system (11) becomes:

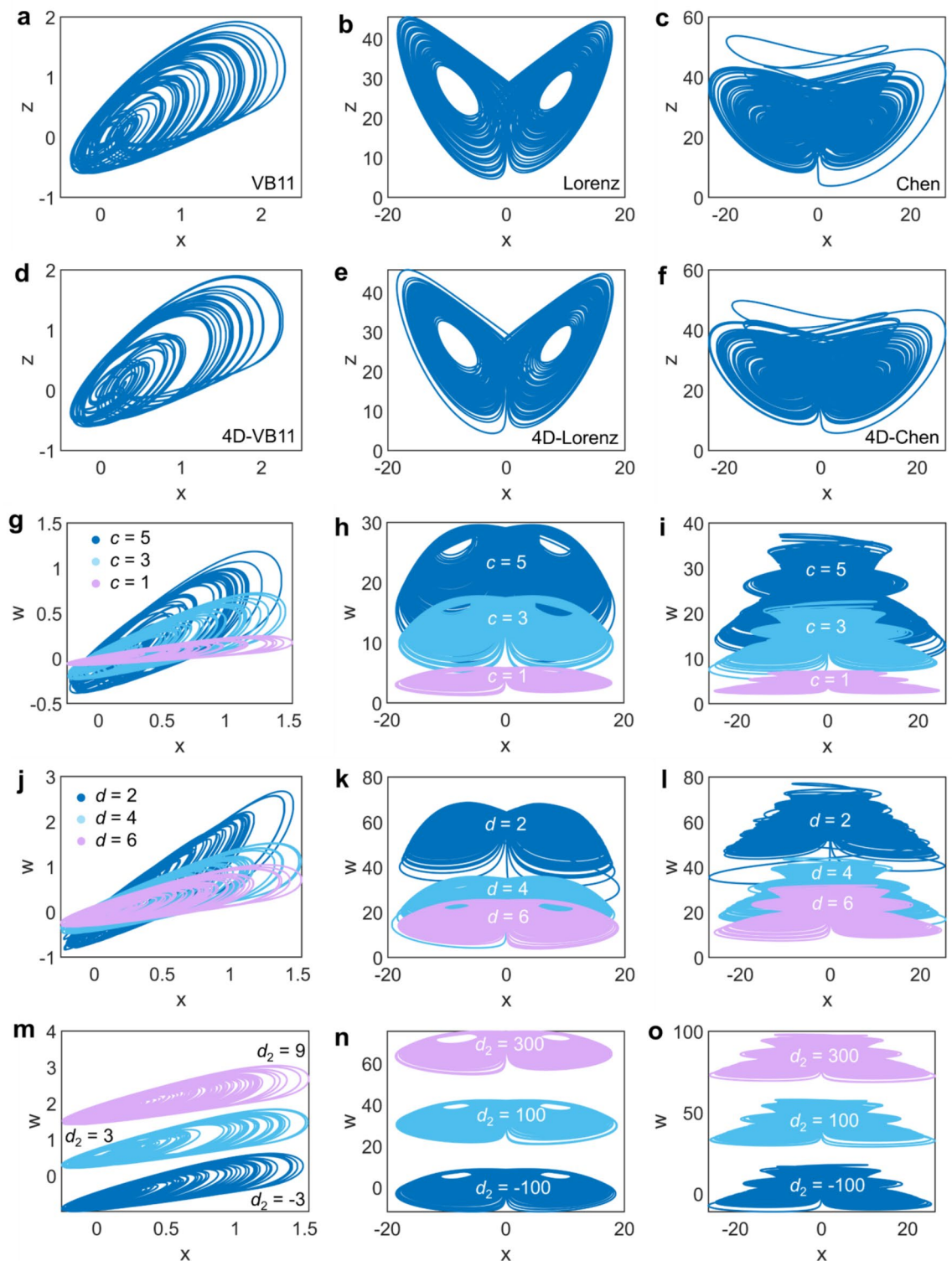


Fig. 1. Construction method for chaotic systems with independent one-dimensional offset functionality with initial values (0.1 0.1 0.1) for 3D-systems, and (0.1 0.1 0.1 0.1) for 4D-systems. Chaotic attractors in the x - z plane of the three-dimensional (a) VB system, (b) Lorenz system, (c) Chen system; Chaotic attractors in the x - z plane for the reconstructed four-dimensional (d) VB system, (e) Lorenz system, (f) Chen system; Influence of parameter c on the structures of (g) VB system, (h) Lorenz system, (i) Chen system; Influence of parameter d on the structures of (j) VB system, (k) Lorenz system, (l) Chen system; Influence of parameter d_2 on the structures of (m) VB system, (n) Lorenz system, (o) Chen system.

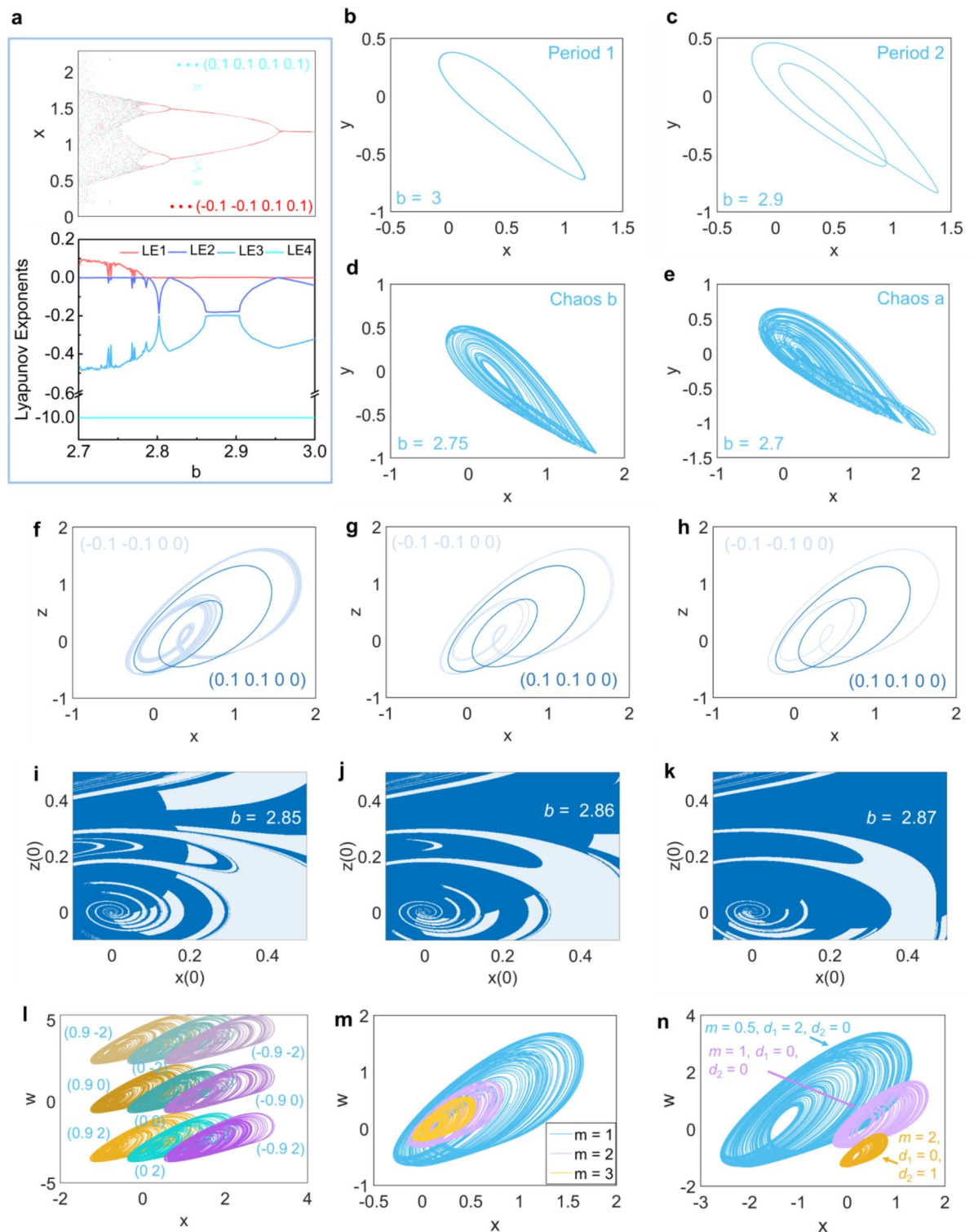


Fig. 2. Dynamic evolution and complete control of a chaotic system. (a) Bifurcation diagram showing system evolution as a function of varying parameter b and the corresponding Lyapunov exponents. (b) Period 1 state when parameter $b=3$. (c) Period 2 state when parameter $b=2.9$. (d) One form of chaotic state when parameter $b=2.75$. (e) One form of chaotic state when parameter $b=2.7$. (f) Coexisting attractors of the system when $b=2.85$. (g) Corresponding basin of attraction of the system on the x - z plane when $b=2.85$. (h) Coexisting attractors of the system when $b=2.86$. (i) Corresponding basin of attraction of the system on the x - z plane when $b=2.86$. (j) Coexisting attractors of the system when $b=2.87$. (k) Corresponding basin of attraction of the system on the x - z plane when $b=2.87$. (l) Amplitude control in the x - w direction. (m) Two-dimensional offset boosting of the attractor in the x - w direction. (n) Complete control of both the amplitude and offset boosting.

$$\begin{cases} \frac{dx}{dt} = y + z \\ \frac{dy}{dt} = my^2 - az \\ \frac{dz}{dt} = x + d_1 + by \\ \frac{dw}{dt} = cz - d(w + d_2) \end{cases} \quad (12)$$

The coefficient m in the last dimension controls the amplitude of the system state variables x , y , z and w without revising the internal variable. The rescaling of the hyperchaotic attractor is realized by the parameter m . The change of m results in a scaling of the state variables x , y , z and w (Fig. 2m). Application of system (12) offers a complete control for system states, enabling precise manipulation of the amplitude and offset through the corresponding non-bifurcation parameters (Fig. 2n). The Lyapunov exponents of the system remain constant when m is varied between $[0, 3]$ (Fig. S2i). These results demonstrate that the variation of parameter m does not change the dynamic behavior of system (12).

To further investigate the effects of amplitude control and offset boosting on the basin of attraction structure of coexistence chaotic attractors, calculations were performed across varying control parameters. These results indicate that, as the amplitude control parameter m is increased, the structure of the attractors will remain unchanged while their amplitudes will be progressively reduced (Fig. 3a-c). Correspondingly, the basin structures underwent gradual compression while preserving their morphological characteristics, indicating that amplitude control can scale the basin without altering its inherent structure (Fig. 3d-f).

In this study, two offset boosting parameters, d_1 and d_2 , were employed to independently control the arbitrary shifts of the corresponding variables x and w , respectively. The computational results pertaining to their associated basins of attraction revealed that as d_1 increased, the basin gradually shifted towards negative values, with no variations for its structure (Fig. 3g-i). A reversal in the direction of this shift was observed when the sign of d_1 was altered, confirming that offset boosting can achieve an overall displacement of the attraction basin.

Furthermore, the basin structure on the x - w plane exhibited a stripe pattern, suggesting that once the parameters x , y , and z are fixed, the value of w has no influence on the structure of coexistence chaotic attractors. This implies that the initial value sensitivity of the system is primarily determined by parameters x , y , and z (Fig. 3j). It is also observed that variations in parameter d_1 can result in a significant x -direction shift of the attraction basin, accompanied by notable structural variations (Fig. 3k). Because the basin of attraction in the w -direction is striped, the overall axial displacement cannot reveal any structural differences in the basin. Therefore, although parameter d_2 actually causes a shift in the system, it appears unchanged due to the consistent structure (Fig. 3l). Overall, amplitude control and offset boosting techniques are found to enable arbitrary scaling and shifting of the basin of attraction without altering the dynamical characteristics of chaotic systems.

Circuit implementation

Chaotic circuits were found to be the most effective means for transforming mathematical chaotic systems into practical electrical signals. In this process, the constants within the differential equation systems were mapped to the resistance values in the circuit, and the bias parameters were controlled by adjusting the DC power supply voltages^{53,54}. The analog electronic circuit of system (12) can be designed for circuit system (13). It is composed of four adders, one multiplier, four inverters and four integrators.

$$\begin{cases} \frac{dx}{dt} = \frac{1}{C_1} \left(\frac{y}{R_1} + \frac{z}{R_2} \right) \\ \frac{dy}{dt} = \frac{1}{C_2} \left(\frac{-z}{R_5} + K \frac{y^2}{R_6} \right) \\ \frac{dz}{dt} = \frac{1}{C_3} \left(\frac{x}{R_9} + \frac{y}{R_{11}} \right) \\ \frac{dw}{dt} = \frac{1}{C_4} \left(\frac{z}{R_{14}} - \frac{w}{R_{15}} \right) \end{cases} \quad (13)$$

where K is the gain coefficient which is equal to 0.1 in system (13). The parameters of the corresponding electronic devices are $C_1 = C_2 = C_3 = C_4 = 10$ nF, $R_1 = R_2 = R_5 = R_9 = R_{10} = R_{16} = 100$ k Ω , $R_6 = 0 \sim 50$ k Ω , $R_{11} = 0 \sim 50$ k Ω , $R_{14} = 8.33$ k Ω , $R_{15} = 10$ k Ω , and $R_7 = R_8 = 10$ k Ω .

The actual chaotic circuit is based on the simulation circuit (Fig. 4a, and Fig. S14), and the corresponding voltage (detected using an oscilloscope) is shown in Fig. 4b-m, and Fig. S3. It is clear that the structure of the electrical signal attractor is fully consistent with the theoretical results calculated by system (12). The system realizes amplitude control (Fig. 4b-j) and offset boosting (Fig. 4k-m). Moreover, the state of the chaotic system can also be regulated by adjustment of the resistance value of resistor R_{11} , which includes period 1 (Fig. 4b-d), period 2 (Fig. 4e-g) and chaos (Fig. 4h-j). It should be noted that an accurate control of CC can be achieved by offset boosting, and the regulation of current density in all the electrodeposition experiments that are presented have been conducted in accordance with this methodology.

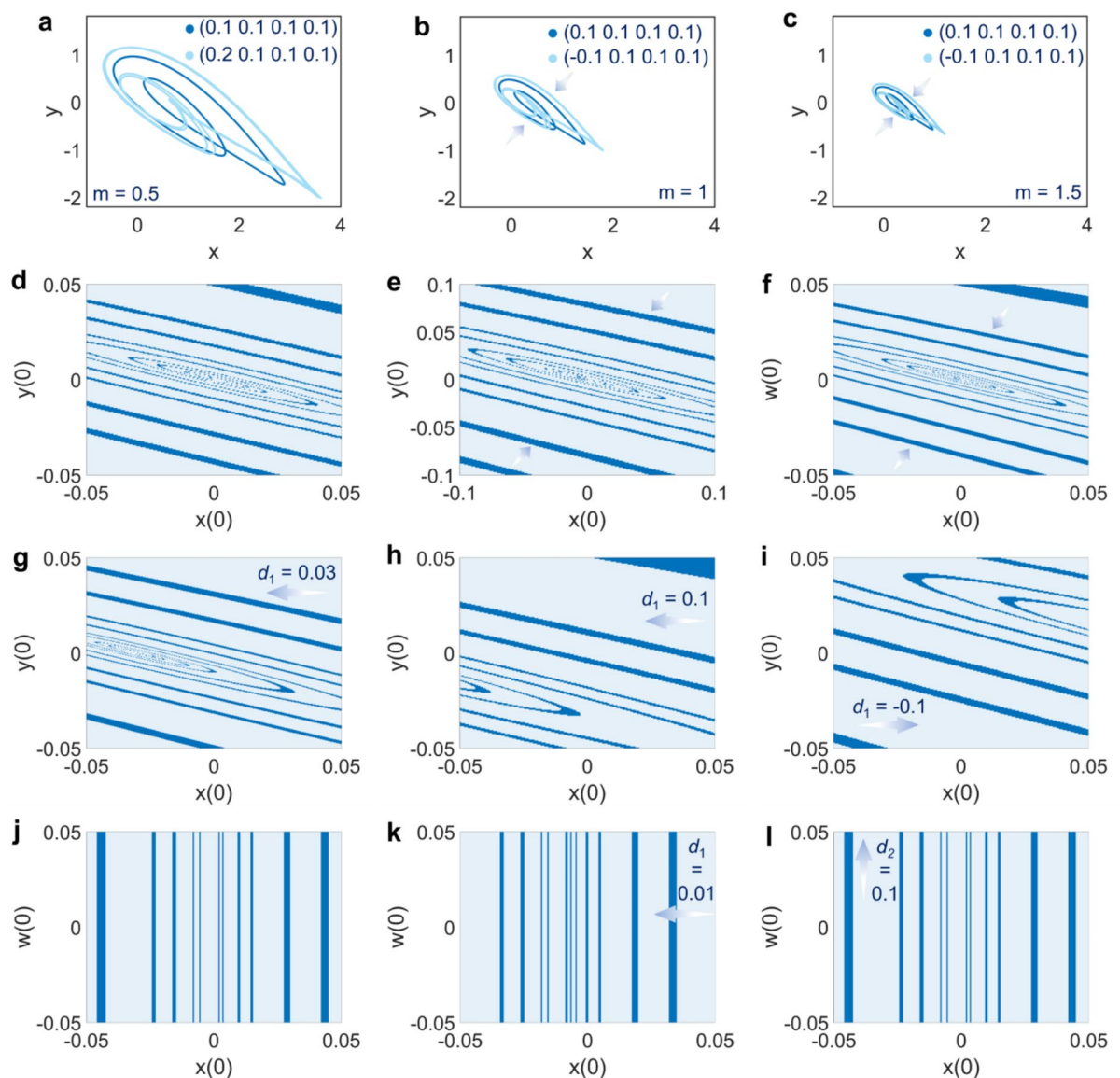


Fig. 3. Attraction basins of the coexisting attractors of cycle 1 and cycle 2 when $a=1$, $b=2.86$, $c=12$, $d=10$. Amplitude control for the coexisting attractors of x - y where (a) $m=0.5$, (b) $m=1$, (c) $m=2$; Effect of amplitude control on the configuration of the attraction basins of x - y with initial values $(x \ y \ 0.1 \ 0.1)$ where (d) $m=0.5$, (e) $m=1$, (f) $m=2$; Effect of offset boosting on attraction basins of x - y where (g) $d_1=0.03$, (h) $d_1=0.1$, (i) $d_1=-0.1$; Effect of offset boosting on attraction basins of x - w with initial values $(x \ 0.1 \ 0.1 \ w)$ where (j) $d_1=d_2=0$, (k) $d_1=0.01$ and $d_2=0$, (l) $d_1=0$ and $d_2=0.1$.

Dynamic regulation of electrodeposition

Electrochemical oscillations

Based on the previous work, the CC manganese metal electrodeposition device has been further improved^{38–40}. Firstly, the overall offset of the voltage waveform on an arbitrary scale is achieved using offset boosting, which in turn enables precise control of the current magnitude, replacing the traditional module of controlling current magnitude by series resistance voltage division (Fig. 5a, and Fig. S15). Secondly, the conventional current and voltage sensing device has been replaced with a new multimeter (UT61E+, Uni-Trend Technology Co., Ltd., China), increasing the sensing range of the current and voltage signals.

The phenomenon of electrochemical oscillations is a typical example of nonlinear kinetic behavior, which reflects the complex physicochemical variations that occur in the system^{55,56}. Consequently, the regulation of electrochemical oscillations represents a regulation of the kinetic behavior of the entire system. Significant electrochemical oscillation electrical signals were detected in the 0.03–0.09 A interval with DC (Fig. 5b–e).

No electrochemical oscillation signals were detected with the use of period 1 (Fig. 5i), period 2 (Fig. 5h), chaos-a (Fig. 5f), and chaos-b (Fig. 5g) currents. This serves to establish that the time-varying current can regulate kinetic behavior during electrodeposition. Furthermore, synchronizing the voltage and current during

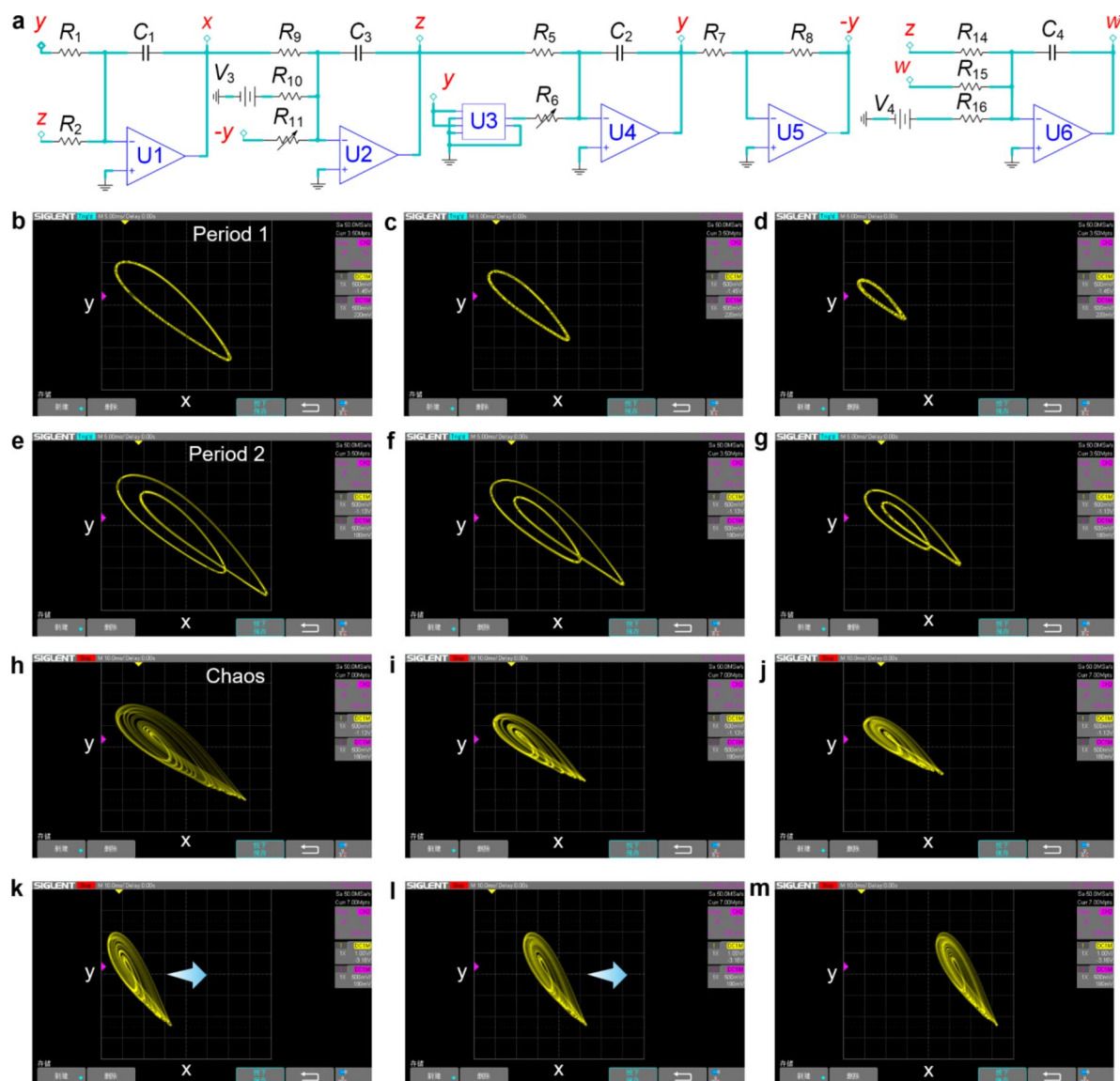


Fig. 4. Complete control of an actual chaotic circuit electrical signal. (a) Electronic schematic of system (13). (b) Amplitude control of system (13) electrical signal waveform in period 1 state when $R_{11} = 30 \text{ k}\Omega$, $R_6 = 40 \text{ k}\Omega$. (c) $R_{11} = 30 \text{ k}\Omega$, $R_6 = 30 \text{ k}\Omega$. (d) $R_{11} = 30 \text{ k}\Omega$, $R_6 = 20 \text{ k}\Omega$. (e) Amplitude control of system electrical signal waveform in period 2 state when $R_{11} = 35 \text{ k}\Omega$, $R_6 = 40 \text{ k}\Omega$. (f) $R_{11} = 35 \text{ k}\Omega$, $R_6 = 30 \text{ k}\Omega$. (g) $R_{11} = 35 \text{ k}\Omega$, $R_6 = 20 \text{ k}\Omega$. (h) Amplitude control of system electrical signal waveform in chaotic state when $R_{11} = 37 \text{ k}\Omega$, $R_6 = 40 \text{ k}\Omega$. (i) $R_{11} = 37 \text{ k}\Omega$, $R_6 = 30 \text{ k}\Omega$. (j) $R_{11} = 37 \text{ k}\Omega$, $R_6 = 20 \text{ k}\Omega$. (k) Offset boosting of system electrical signal waveform in chaotic state when $R_{11} = 37 \text{ k}\Omega$, $R_6 = 40 \text{ k}\Omega$ with 0 V offset voltage. (l) 2 V offset voltage. (m) 4 V offset voltage.

the electrochemical oscillation test has revealed that the time-varying current can reduce the voltage to current ratio when compared with DC. Moreover, the voltage-to-current ratio can be decreased with an increased current density, consistent with the non-linear nature of electrodeposition (Fig. 5j). It can be concluded that the voltage/current ratio of the chaotic state is lower than the period state.

Effect of current density

As the ions in solution are consumed continuously during the electrodeposition of manganese metal, the properties of the electrode plate are also transformed. The current (Fig. 6a, d) and voltage (Fig. 6b, e) signals generated during electrodeposition were collected and the average value calculated to ensure accurate calculated CE and EC data. The results indicate that the fluctuation range of current and voltage signals in the chaotic circuit is clearly greater (Fig. 6g, h). The CC voltages and currents employed in these experiments exhibit an overall shift to the upper portion of the slope³⁹ (Fig. 6c). This response demonstrates that an overall shift of the currents and voltages can be achieved by offset boosting. Furthermore, the voltage-current signals through phase-space reconstruction of the DC electrolysis experiments with various current densities demonstrate that the range of

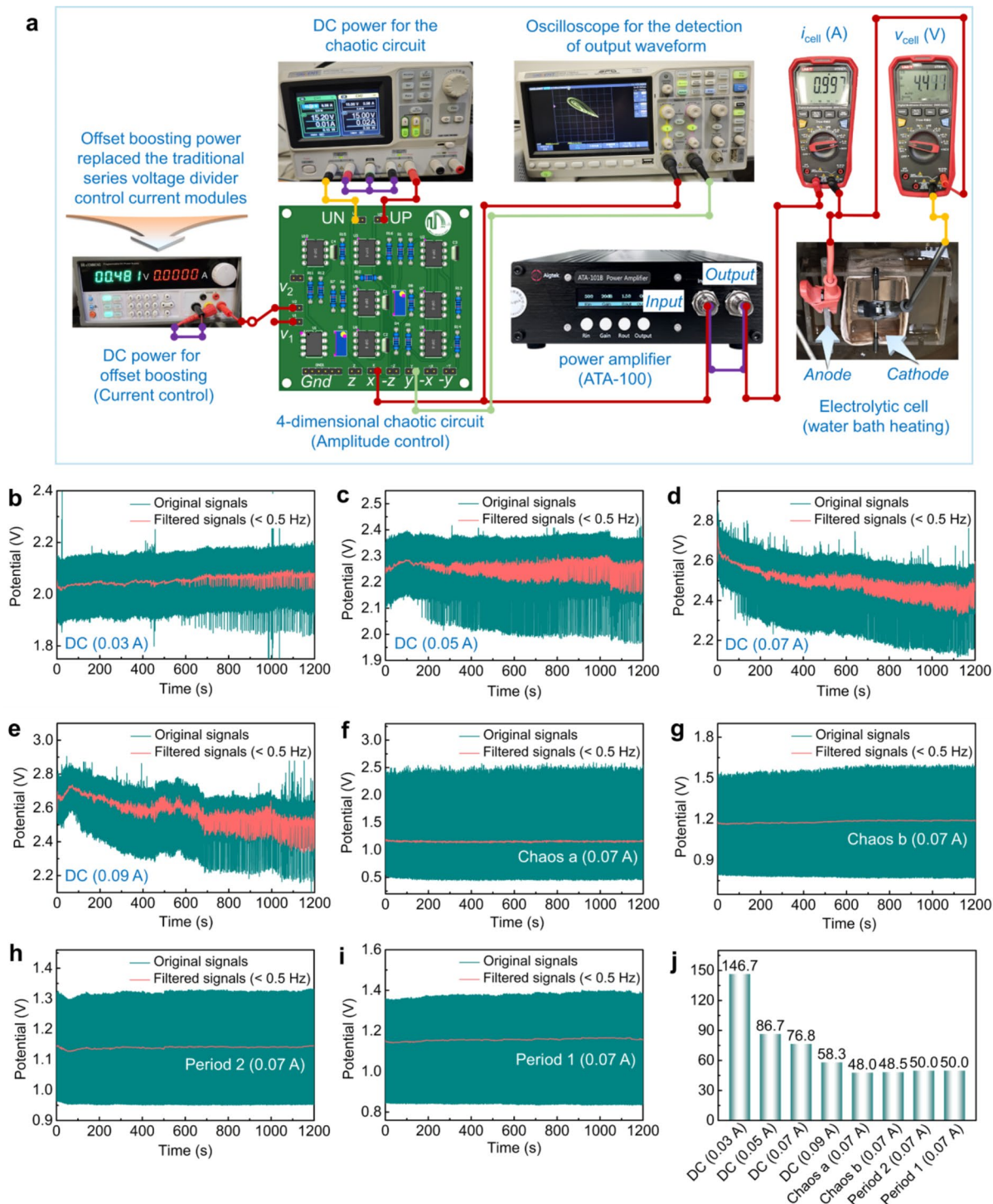


Fig. 5. Chaotic power integration and kinetic behavior regulation for manganese electrodeposition employing various currents. **(a)** Experimental set-up for electrodeposition by chaotic power. **(b)** Electrochemical oscillatory signals with DC for 0.03 A. **(c)** DC for 0.05 A. **(d)** DC for 0.07 A. **(e)** DC for 0.09 A. **(f)** Electrochemical oscillatory signals with chaotic-a current for 0.07 A. **(g)** Chaotic-b current for 0.07 A. **(h)** Period 2 current for 0.07 A. **(i)** Period 1 current for 0.07 A. **(j)** Ratio of the voltage to current during the entire electrochemical oscillation testing process.

voltage fluctuations under the influence of elevated current densities is amplified (Fig. 6f). This phenomenon may be attributed to an intensified reaction and accelerated rate of ion depletion at higher currents. To accurately quantify the fluctuation ranges of currents and voltages, the range of electrical signals at various current densities was calculated. This has substantiated the exceptionally wide fluctuation range of chaotic currents (Fig. 6g, h).

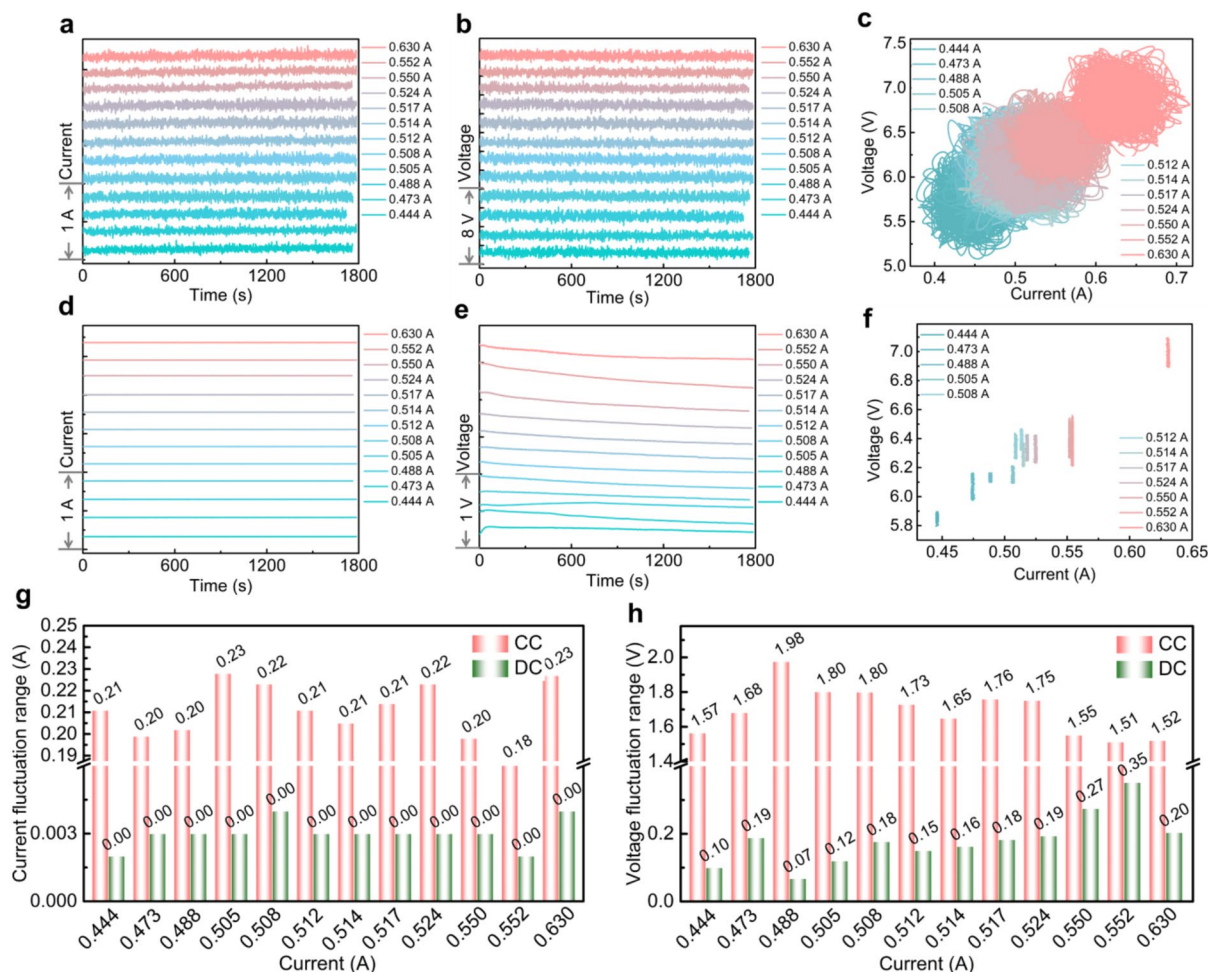


Fig. 6. Signal characteristics of various current densities in manganese metal electrodeposition systems. (a) Chaotic current signals. (b) Chaotic voltage signals. (c) Correlation of the current and voltage of chaotic power. (d) Direct current signals. (e) Direct voltage signals. (f) Correlation of the current and voltage of DC. (g) Current fluctuation range for the two forms of power. (h) Voltage fluctuation range for the two forms of power.

In terms of cost reduction, it is significant that the CE can be improved and EC reduced by CC over a wide range (1110 A/m²–1575 A/m²) of current densities (Fig. 7a, b). The voltage/current ratio during actual manganese metal electrodeposition has demonstrated that the increased current efficiency of chaotic currents can be attributed to a reduction of the cell voltage (Fig. 7c). The results of the area distribution of manganese nodules calculated using image processing have revealed that CC can achieve a significant suppression of nodules over a wide range of current density variations (Fig. S4a–d). The reduced area ratio of nodules (AR-N) was found to exceed 40%, with a maximum of 48.8% (Fig. 7d).

To more accurately evaluate the specific variations of improved CE and enhanced EC, the reduced ratio of voltage to current and area of nodules was calculated (Fig. 7e, f). The results have shown that the trends with respect to CE and EC exhibit peaks, indicating an optimal range of current density for chaotic electrolysis. When the average current under CC was set to 0.508 A, the CE can be improved by 6.08%, the EC can be lowered by 0.84 kWh/kg, the ratio of voltage to current can be reduced by 0.4, and the area ratio of nodules can be inhibited by 40.5%, which represents the best result reported to date^{39,40}.

Effect of the waveform

The amplitude of the chaotic signal can also be controlled by adjustment of the amplification factor of the power amplifier. The amplification factor of the output voltage is represented by 14 dB (voltage amplification by 14 times) and 4 dB (4 times). The influence of voltage fluctuation amplitude and the waveform on the electrodeposition process of manganese metal was evaluated at 4 dB and 14 dB with five types of waveforms (period 1, period 2, chaos-a, chaos-b, and DC).

The current signals and voltage signals are illustrated in Fig. 8a, b, respectively, with a gain of 14 dB. When the gain was 4 dB, the corresponding current and voltage signals are depicted in Fig. 8d, e. These results demonstrated that the amplitude of the current and voltage can be modulated by power amplifiers, and the pattern of voltage

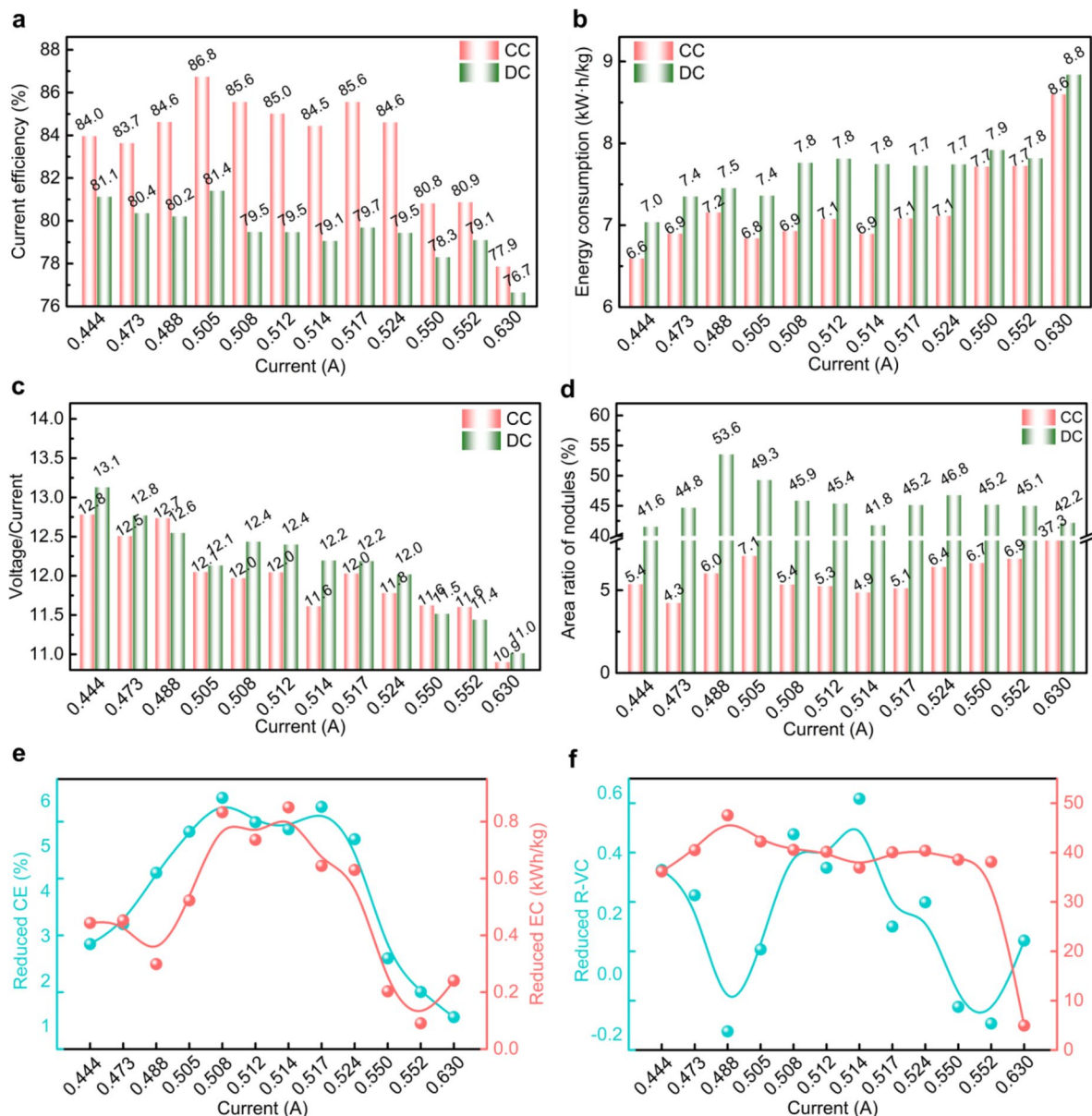


Fig. 7. The relationship between current efficiency, energy consumption, ratio of voltage to current, and area ratio of nodules with $2 \times 2 \text{ cm}^2$ plates for various current densities. **(a)** Current efficiency. **(b)** Energy consumption. **(c)** Ratio of voltage to current. **(d)** Area ratio of nodules. **(e)** Improved current efficiency and lower energy consumption. **(f)** Reduced ratio of voltage to current and the reduced area ratio of nodules.

fluctuation range variation aligns consistently with the current variation. To better compare the fluctuation ranges and correlations of current signals and voltage signals under various types of current excitations, the reconstructed phase space of the signals was plotted with the current signals taken as the abscissa and the voltage signals as the ordinate (Fig. 8c, f). The impact of the electrical signal waveform on the final output working current is significant. It can be concluded that chaotic signals result in greater current fluctuations, while the fluctuation range of periodic current is smaller. This response provides an additional rationale for the greater efficiency of CC in the electrodeposition of manganese when compared with DC.

For a more precise assessment of current and voltage fluctuation ranges, the ranges (The differences between maximum and minimum values) of both current and voltage signals were calculated during the electrodeposition process. It is clear that, under constant direct current (DC) mode, the fluctuation range of the current signal remains below 0.01 A during electrodeposition (Fig. 9a). Conversely, when a chaotic current is employed, the current fluctuation range can extend to 0.25 A, with a corresponding voltage fluctuation of 2.03 V (Fig. 9a, b). Significantly, this fluctuation range can be finely tuned by adjusting the gain factor of the power amplifier. The influence of the voltage fluctuation amplitude on CE is greater than the impact of the waveform (Fig. 9c, and Fig. S5c). A wider voltage fluctuation range is more conducive to manganese electrodeposition. On the other hand, a chaotic waveform with a more complex structure can result in a larger fluctuation range of the output current,

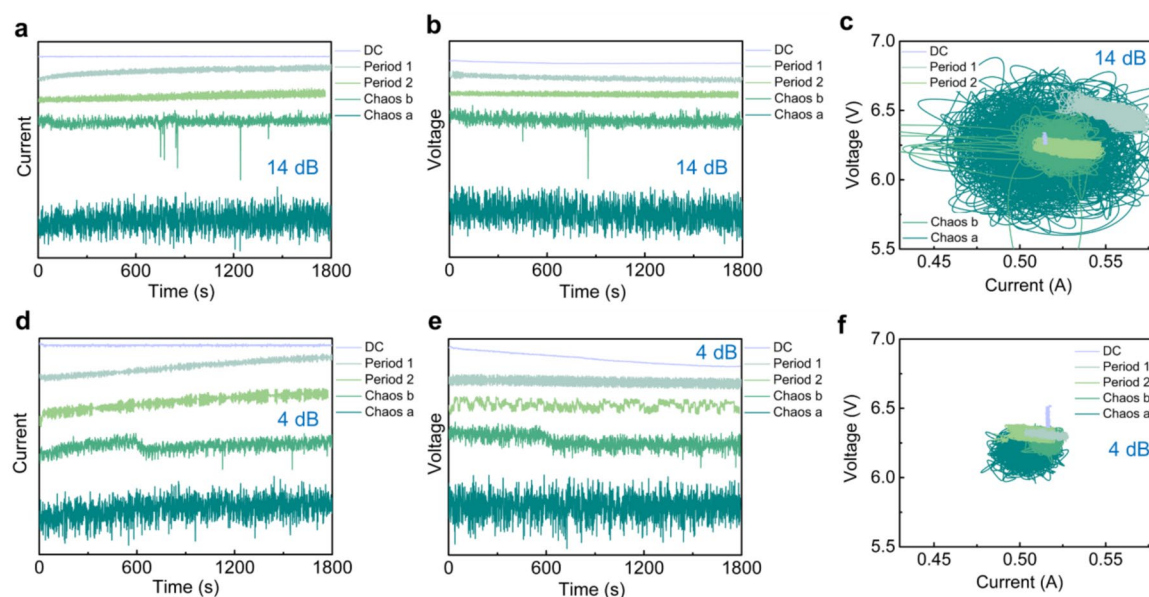


Fig. 8. Signal characteristics of various currents in manganese metal electrodeposition systems. (a) Chaotic current signals amplified by a 14 dB power amplifier. (b) Chaotic voltage signals amplified by a 14 dB power amplifier. (c) Correlation of the current and voltage of chaotic power amplified by a 14 dB power amplifier. (d) Chaotic current signals amplified by a 4 dB power amplifier. (e) Chaotic voltage signals amplified by a 4 dB power amplifier. (f) Correlation of the current and voltage of chaotic power amplified by a 4 dB power amplifier.

which improves CE relative to a periodic electrical signal. The energy consumption should consider both current efficiency and cell voltage, where the chaotic electrical signal with a large fluctuation range demonstrates the most favorable effect (Fig. 9c-e, and Fig. S5d, e). The value of reduced EC can reach 0.58 kWh/kg compared with DC electrolysis.

To demonstrate the relationship between the growth of manganese nodules and CE, nodule distribution area and microscopic tests were carried out on manganese metal products under the action of different waveforms and amplitudes (Fig. 9g-j). It is evident that the manganese nodules can be almost completely inhibited by the current with a high fluctuation range (Fig. 9g, h), which serves to reduce the ratio of nodules by at least 26% (Fig. 9f, and Fig. S5a, b, f).

This effect is corroborated by microscopic observations, where there were no discernible spherical manganese nodules in all regions of the deposited manganese metal in the case of large fluctuating ranges of currents (Fig. 9i, j, and Fig. S6). In contrast, a considerable number of spherical manganese nodules were observed in all regions of the manganese metal following electrolysis by DC or CC with low fluctuating ranges. These findings are consistent with the proposal that manganese nodules are the main cause of energy dissipation during electrodeposition.

Effect of electrodeposition time

The effect of time was assessed in comparative tests with various electrodeposition times. The fluctuation range of current signals showed little variation with the duration of electroplating (Fig. S7a, d). Moreover, the fluctuation range of chaotic current-voltage signals and the attractors identified in phase space reconstruction consistently demonstrated the stability of the fluctuation range of chaotic electrical signals (Fig. S7b, c). The cell voltage decreased continuously with increasing electrodeposition time by DC (Fig. S7e, f). The increasing specific surface area of the manganese metal as it is continuously deposited on the stainless-steel electrode plate may account for this effect. It should be noted that the amplitude of the CC and voltage fluctuations also increased with time (Fig. S7g, h, and Fig. S8).

The CE results demonstrate that the electrodeposition time exerts a significant influence on the manganese metal electrodeposition process. The CE shows a decreasing tendency with increased electrodeposition time. This may be attributed to a continuous depletion of manganese ions. The current efficiency of CC electrolysis is 6.13% higher than DC electrolysis at an electrodeposition time of 30 min. In contrast, the current efficiency of CC electrolysis is 4.34% lower than DC electrolysis at an electrodeposition time of 120 min (Fig. 10a, d). The data for energy consumption align with the CE results (Fig. 10b, e). The application of CC can reduce energy consumption by 0.95 kWh/kg for an electrodeposition time of 30 min. The ratio of voltage to current (R-VC) results indicate that the chaotic power can reduce the cell voltage (Fig. 10c).

It is evident that the growth of manganese metal nodules is significantly inhibited by the CC, with a minimum of 26% inhibition when compared with DC electrolysis, and a 47% inhibition for an electrodeposition time of 120 min (Fig. 10f).

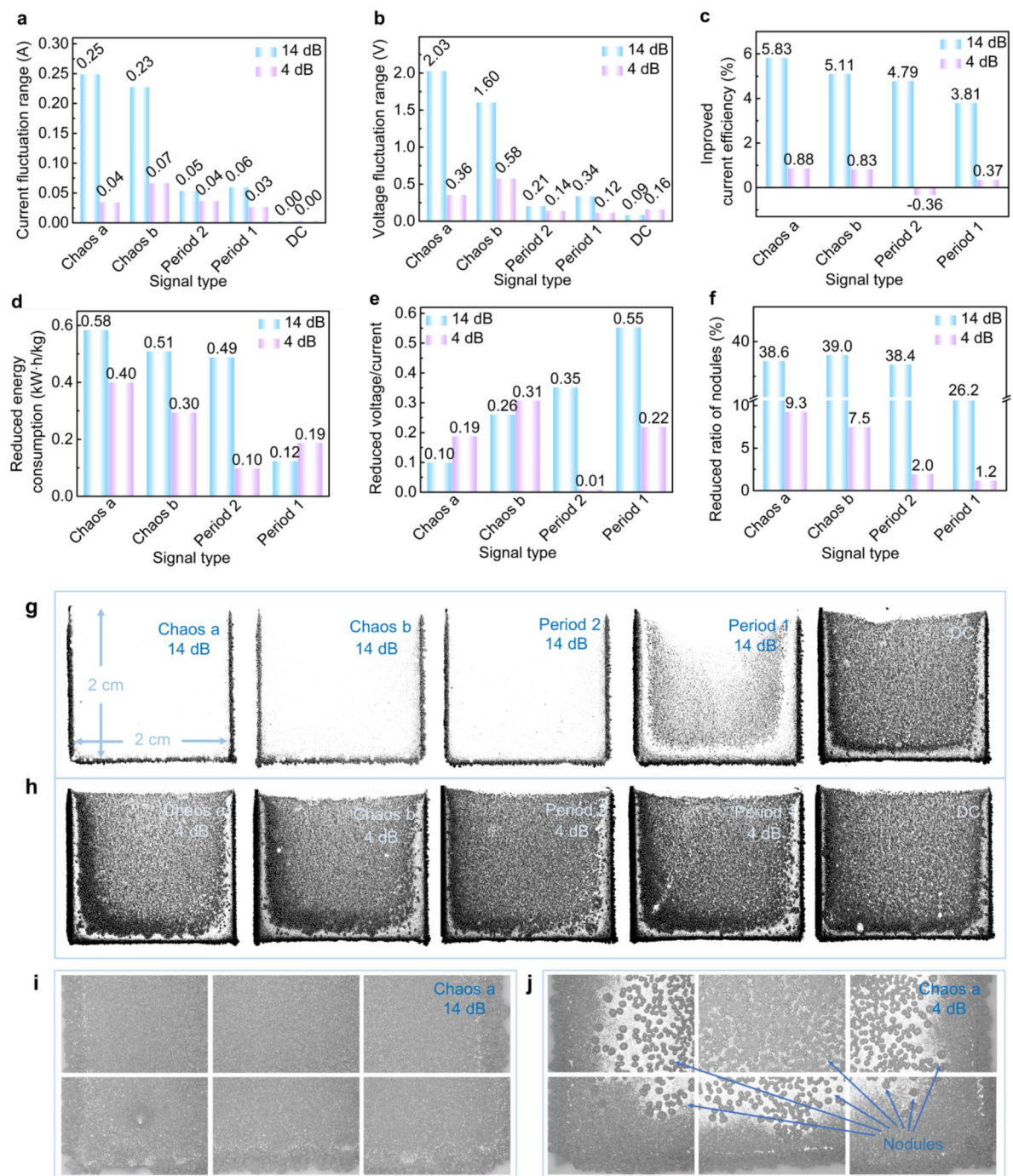


Fig. 9. Signal characteristics, current efficiency, energy consumption and the distribution of nodules for current waveforms. **(a)** Current fluctuation range for the two forms of power. **(b)** Voltage fluctuation range. **(c)** Enhanced current efficiency by CC compared with DC. **(d)** Reduced energy consumption compared with DC. **(e)** Reduced ratio of the voltage to current. **(f)** Reduced area ratio of nodules. **(g)** Distribution of manganese nodules by time-varying current amplification to 14 dB. **(h)** Distribution of manganese nodules by the time-varying current amplification to 4 dB. **(i)** Microscopy images of manganese metal with chaotic-a current amplified to 14 dB. **(j)** Microscopy images of manganese metal with chaotic-a current amplified to 4 dB.

The results of the distribution of manganese nodules after the binarized extraction (Fig. 10g, h), and the corresponding optical microscopy analysis have corroborated the findings of the area calculations for the manganese nodules (Fig. 10i, j). A considerable number of nodules are distributed throughout the manganese metal electrode plates by DC.

Microscopic analysis was conducted at higher magnitude to obtain greater detail regarding the growth, morphology and evolution of manganese nodules with time in the middle part of the electrode plate (Fig. 11). The

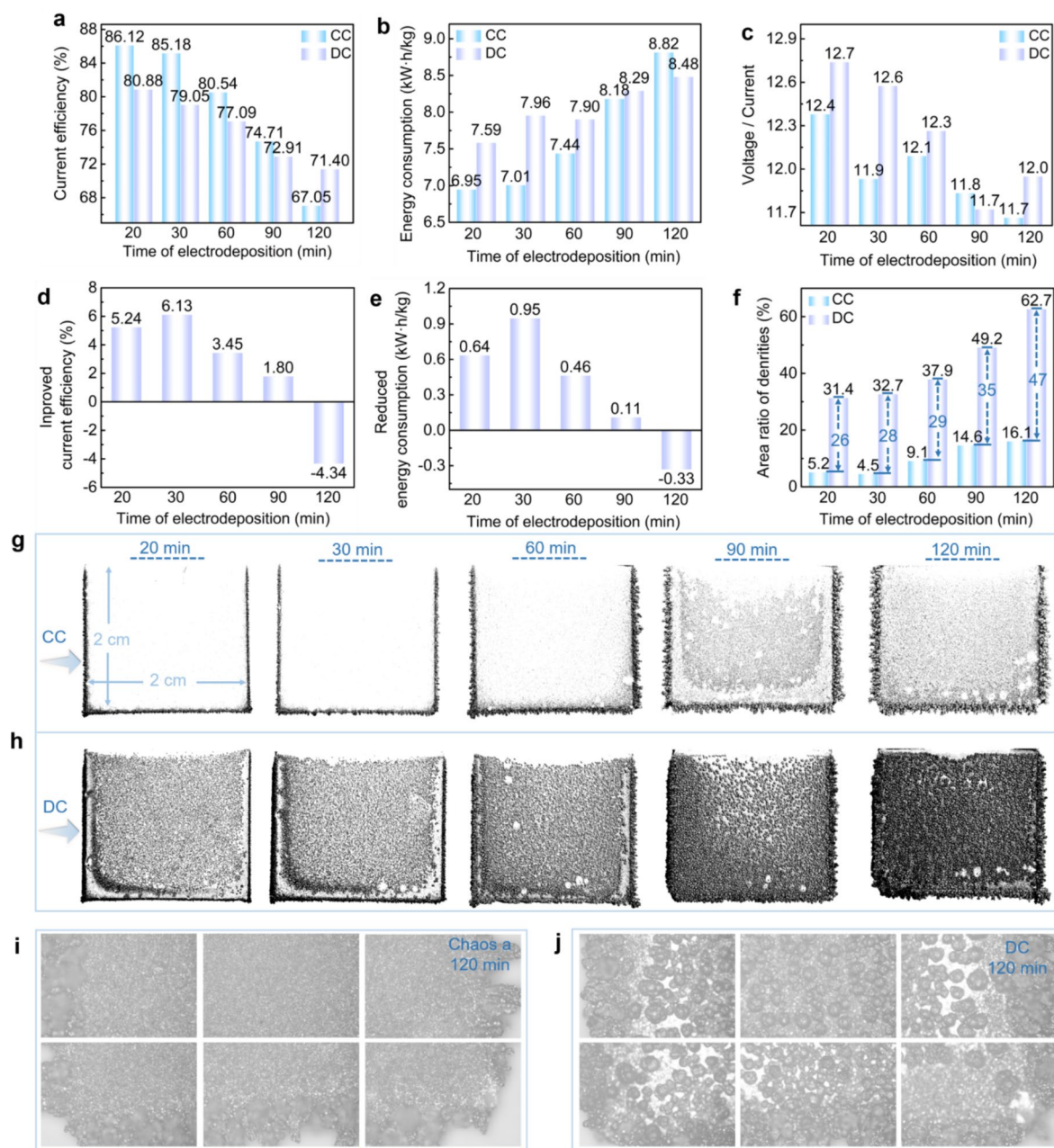


Fig. 10. Energy consumption during the electrodeposition of manganese metal and associated current efficiency, voltage-current ratio, and the nodule distribution for various times. **(a)** Current efficiency. **(b)** Energy consumption. **(c)** Ratio of voltage to current. **(d)** Improved current efficiency by CC compared with DC. **(e)** Reduced energy consumption. **(f)** Reduced area ratio of nodules. **(g)** Distribution of manganese nodules with CC. **(h)** Distribution of manganese nodules with DC. **(i)** Microscopy images of manganese metal by CC after 120 min. **(j)** Microscopy images of manganese metal by DC after 120 min.

results of a statistical analysis of nodule particle size have demonstrated that the manganese nodules exhibited a continuous increase from a value of 36.6 μm (20 min) to a final 142.6 μm (120 min) with DC (Fig. 11c, f, i, l, o).

Scanning electron microscopy (SEM) analysis of the manganese metal deposited at different times on a smaller scale was also conducted. It can be seen that the manganese metal deposited by CC consists of small-scale spherical particles that accumulate as a very dense crystal growth (Fig. 12a, c, e, g, i). Conversely, the surface of manganese metal deposited by DC electrodeposition is characterized by the presence of a considerable larger-scale spherical manganese nodule component (Fig. 12b, d, f, h, j). Moreover, the structural units of manganese metal constituting the spherical manganese nodules are demonstrably distinct from the manganese metal deposited by CC electrodeposition. Furthermore, the SEM analysis has established that the spherical manganese nodules were formed over time.

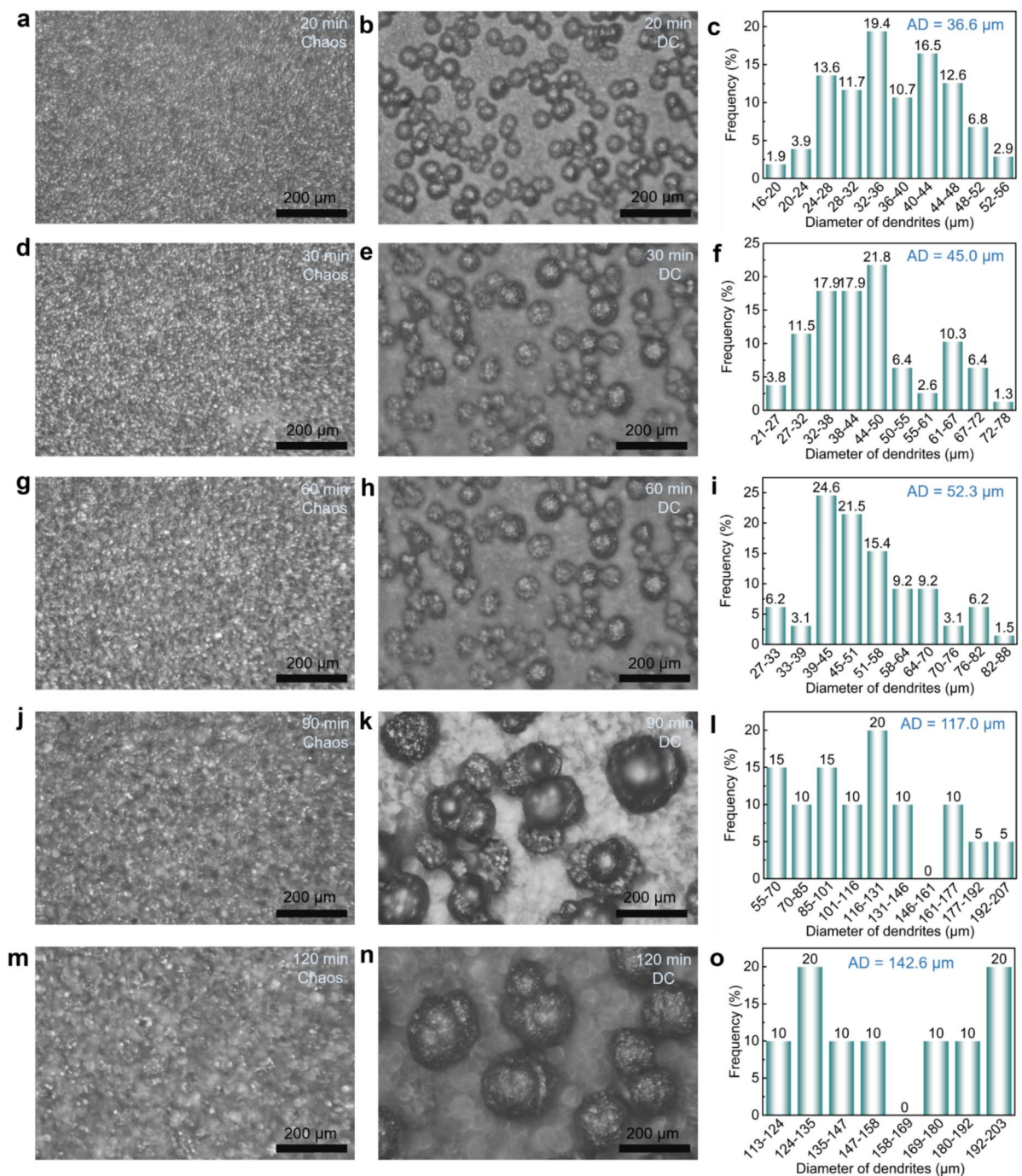


Fig. 11. Morphology of the manganese metal from optical microscopy analysis of the central part of the electrode plate. (a) Chaos-a current for 20 min. (b) DC for 20 min. (c) Particle size distribution of manganese nodules with DC for 20 min (AD denotes average diameter). (d) Chaos-a current for 30 min. (e) DC for 30 min. (f) Particle size distribution with DC for 30 min. (g) Chaos-a current for 60 min. (h) DC for 60 min. (i) Particle size distribution with DC for 60 min. (j) Chaos-a current for 90 min. (k) DC for 90 min. (l) Particle size distribution with DC for 90 min. (m) Chaos-a current for 120 min. (n) DC for 120 min. (o) Particle size distribution with DC for 120 min.

The phase composition of electrodeposited manganese metal at different times was assessed by XRD analysis (Fig. 12k). The predominant physical phase was manganese metal, with the most prominent characteristic peak attributed to the (330) crystal plane. It should be noted that the intensity of the (330) diffraction peak decreased under the influence of a chaotic power supply, suggesting that the physical phase composition of the manganese metal has undergone a transformation. In contrast, there was no significant difference in the intensity of the diffraction peaks under DC electrolysis (Fig. 12l). In addition, the intensity of all the characteristic peaks before

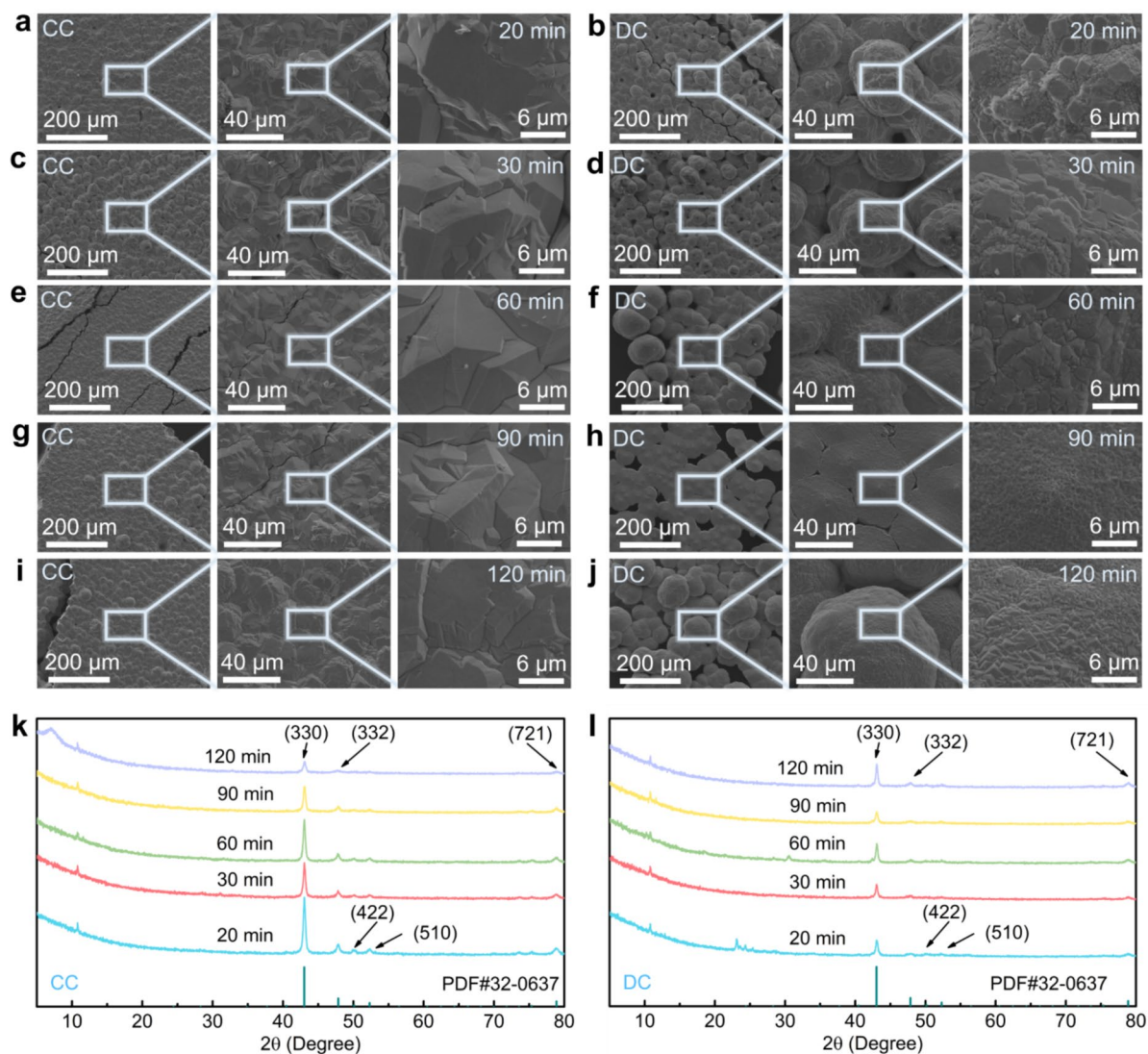


Fig. 12. Morphology and physical composition of manganese metal from SEM and XRD analysis. **(a)** SEM images of manganese metal by CC for 20 min. **(b)** SEM images of manganese metal by DC for 20 min. **(c)** SEM images of manganese metal by CC for 30 min. **(d)** SEM images of manganese metal by DC for 30 min. **(e)** SEM images of manganese metal by CC for 60 min. **(f)** SEM images of manganese metal by DC for 60 min. **(g)** SEM images of manganese metal by CC for 90 min. **(h)** SEM images of manganese metal by DC for 90 min. **(i)** SEM images of manganese metal by CC for 120 min. **(j)** SEM images of manganese metal by DC for 120 min. **(k)** XRD patterns of manganese metal by CC for various times. **(l)** XRD patterns of manganese metal by DC for various times.

90 min was lower than that associated with manganese metal electrodeposited by CC. This result provides further evidence that the crystal structure of manganese nodules differs from that of manganese metal, and demonstrates that a chaotic power supply can be used to modulate the crystal structure of manganese metal.

A denser Mn metal is more resistant to oxidation, increasing purity and reducing the necessity for passivation solutions. X-ray photoelectron spectroscopy (XPS) analysis was conducted on the manganese metal products deposited at various times. The results have indicated that the principal impurity elements present are N, S, and Cr (Fig. 13a–d). The manganese element content of the product generated by CC is higher than DC. Chromium was not detected for the CC electrodeposition products (Fig. 13c). In contrast, the presence of chromium was identified at 20 min, 30 min and 120 min by DC deposition (Fig. 13d). This indicates that the CC deposited manganese metal is denser, which subsequently reduces the residual chromium. It is well established that chromium is a highly toxic pollutant⁵⁷. The development of chromium-free passivation techniques represents a significant challenge in the electrodeposition industry. The advent of CC electrodeposition offers a promising avenue for the advancement of chromium-free passivation research⁵⁸.

The XPS peaks due to surface oxygen on the manganese metal surfaces were deconvoluted and fitted. It is evident that the intensity of the surface oxygen peaks at lower energy levels diminishes gradually with prolonged chaotic circuit electrodeposition (Fig. 13e). In contrast, the surface oxygen peaks for DC electrodeposited

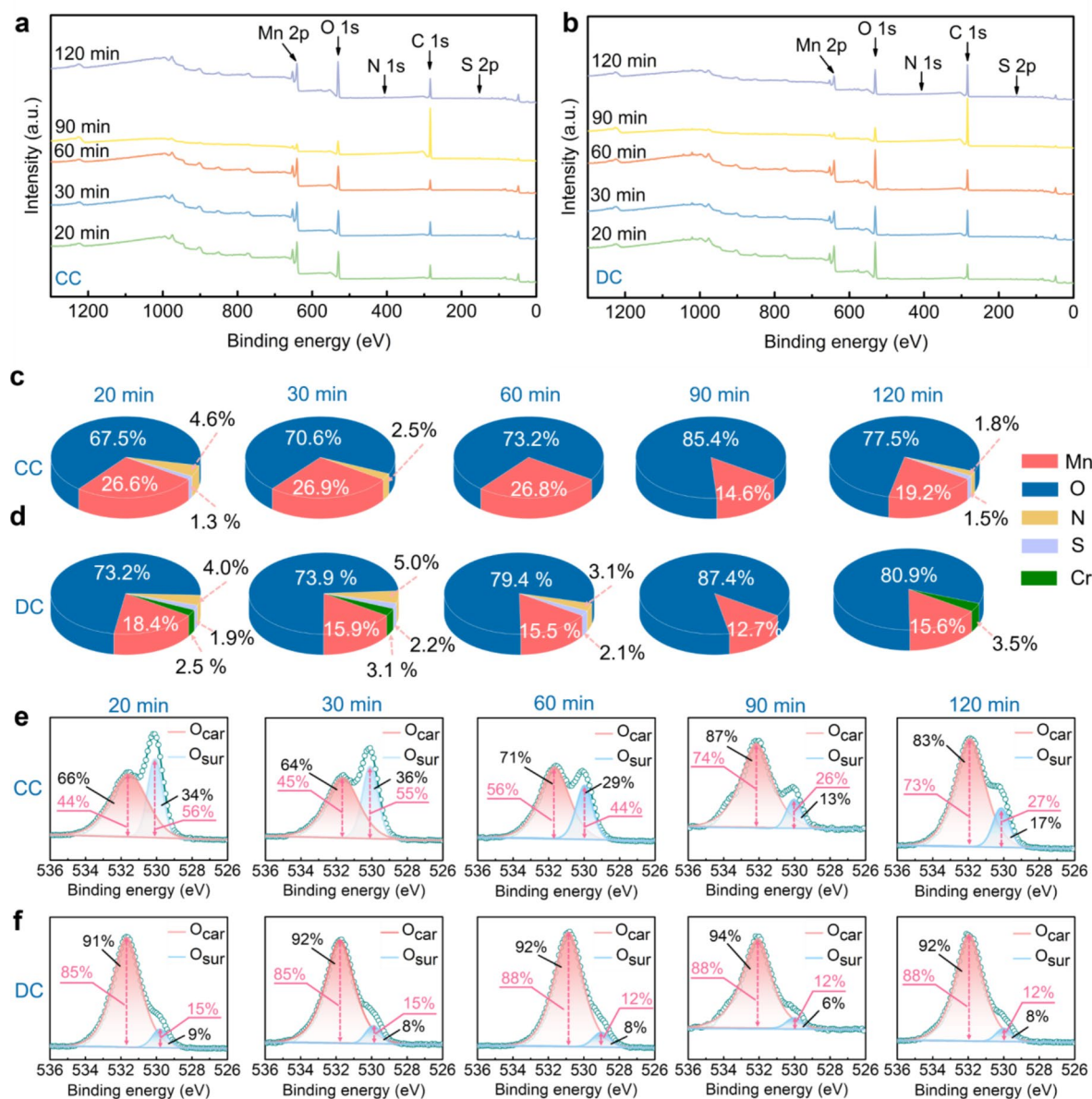


Fig. 13. Elemental distribution and valence distribution of manganese metal generated at various times and currents. **(a)** XPS full spectrum of manganese metal by CC for various times. **(b)** XPS full spectrum of manganese metal by DC for various times. **(c)** Elemental composition of Mn metal by CC. **(d)** Elemental composition of Mn metal by DC. **(e)** XPS spectra for oxygen with peak deconvolution and fitting associated with Mn metal by CC. **(f)** XPS spectra for oxygen with peak deconvolution and fitting associated with Mn metal by DC.

manganese metal were consistently low in intensity, appreciably lower than those obtained from CC electrodeposition (Fig. 13f).

Electrodeposition amplification experiment

This study has also considered the potential applications of this technology in industry, employing a high-power current amplifier to achieve CC amplification on a larger scale (1 A). The current and voltage signals over the entire electrolysis process have also been collected (Fig. S9). The range of current and voltage fluctuations of the chaotic power under high current was much greater than that of DC power (Fig. 14a, b). The ratio of voltage to current with CC was lower relative to DC (Fig. 14c).

The application of CC enabled an increase in current efficiency with energy saving (Fig. 14d, e). It is also evident that CC resulted in a reduction in nodule content, where microscopy analysis has established a close relationship between energy consumption and nodule formation (Fig. 14f–j, Fig. S10, and Fig. S11). An analysis of manganese metal cross-sections by SEM has established enhanced metal deposition by CC, which may be linked to the energy component dissipated by the manganese nodules in the case of DC (Fig. 14k, l, and Fig. S12).

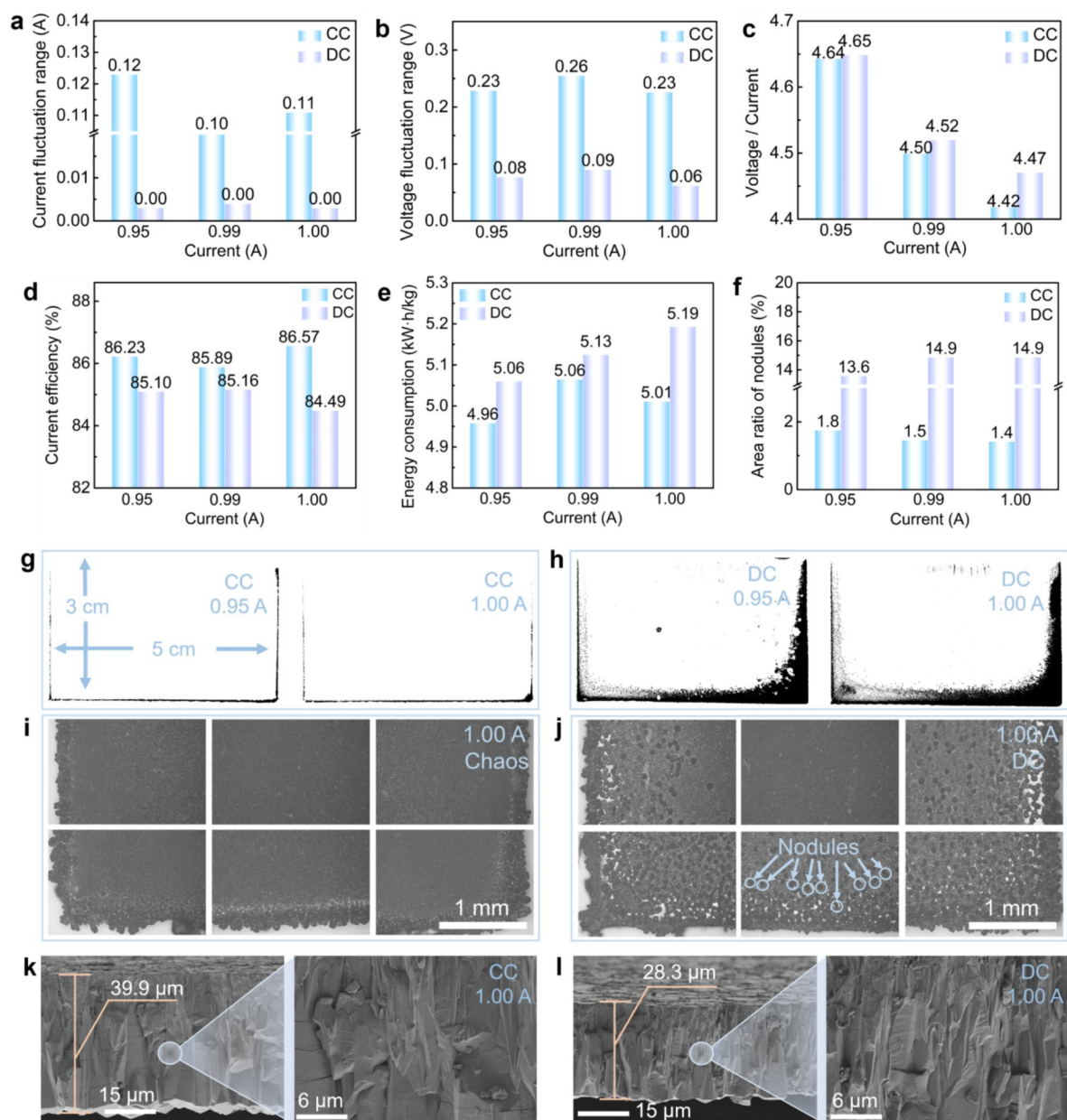


Fig. 14. Energy consumption and the relationship with current efficiency, signal properties, nodule distributions, and thickness of Mn metal generated for larger current scale using the power amplifier (FPA 101). **(a)** Current fluctuation for the two forms of current. **(b)** Voltage fluctuation. **(c)** Comparison of the ratio of voltage to current. **(d)** Current efficiency. **(e)** Energy consumption. **(f)** Area ratio of nodules. **(g)** Nodules distribution with CC. **(h)** Nodules distribution with DC. **(i)** Morphology of manganese metal with CC using optical microscopy. **(j)** Morphology of manganese metal with DC. **(k)** Cross-section SEM images of manganese metal by CC. **(l)** Cross-section SEM images of manganese metal by DC.

Effect of electrodeposition time on anode mud

To ascertain whether the physicochemical properties of the by-products formed during electrodeposition undergo a similar transformation, a SEM analysis was conducted on the anode residue or “mud”. The microstructural composition of the anode mud is complex, but some obvious variations are apparent with increased electrodeposition time (Fig. S13)⁵⁹. Applying a 40 μm scale, it can be seen that the anode mud consists of a large number of spherical particles and manganese dioxide particles characterized by a much smaller spherical structure. It should be noted that the anodic mud deposited under chaotic currents appears to contain a greater proportion of spherical manganese dioxide.

The electrodeposition products at the anode were subjected to TEM analysis (Fig. 15a–f). The high-resolution TEM (HRTEM) images reveal that the anodic by-products are very complex with a range of lattice spacings, suggesting at least three crystal structures (Fig. 15b, e). A spacing of 0.297 nm may be ascribed to β -MnO₂.

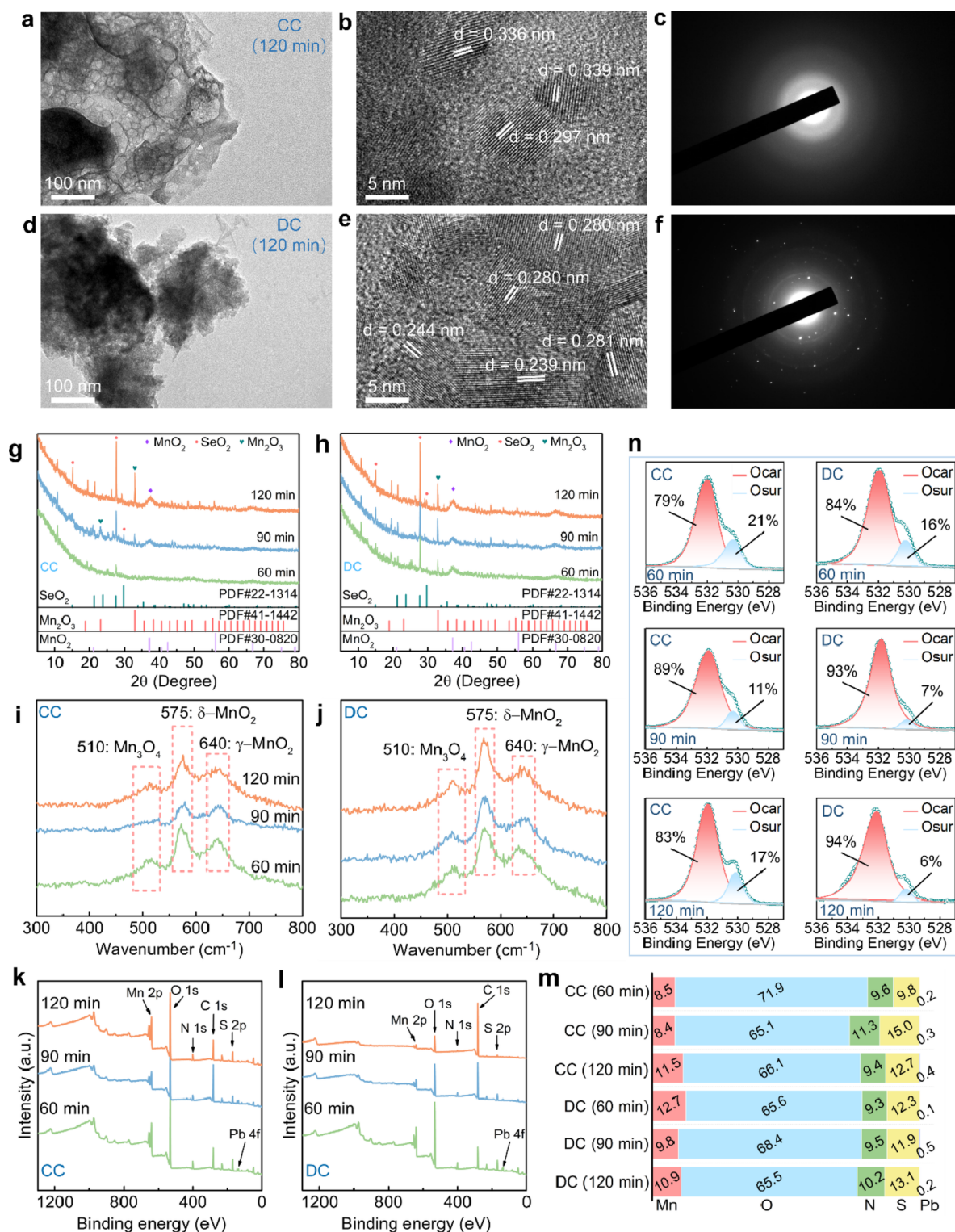


Fig. 15. Physicochemical properties of the anode mud for various times and current types. **(a)** TEM image of the anode mud with CC for 120 min. **(b)** High-resolution TEM image of the anode mud with CC. **(c)** Broad halo ring in the SAED pattern indicating amorphous character the anode mud with CC. **(d)** TEM image of the anode mud with DC for 120 min. **(e)** High-resolution TEM image of the anode mud with DC. **(f)** Broad halo ring in the SAED pattern indicating polycrystalline character of the anode mud with DC. **(g)** XRD patterns of the anode mud with CC. **(h)** XRD patterns of the anode mud with DC. **(i)** Raman spectra of the anode mud with CC. **(j)** Raman spectra of the anode mud with DC. **(k)** XPS survey scan of the anode mud with CC. **(l)** XPS survey scan of the anode mud with DC. **(m)** Elemental distribution in the anode mud. **(n)** XPS O1s spectrum with peak fitting.

or δ -MnO₂ according to previous research^{60,61}. The crystal spacings of 0.336 nm and 0.339 nm are between β -MnO₂ and γ -MnO₂⁵⁹. Two distinct lattice fringes of 0.280 nm and 0.281 nm are consistent with the lattice framework of Mn₃O₄^{62,63}. In addition, the lattice fringes of 0.239 nm and 0.244 nm may be attributed to β -MnO₂⁶¹. The broad halo ring in the selected area electron diffraction (SAED) pattern provides evidence that the sample of CC anode mud includes an amorphous component (Fig. 15c). The halo ring observed in the SAED pattern for the DC anode mud is indicative of polycrystalline material (Fig. 15f). These results confirm that hyperchaotic current can regulate the crystal structure of the anode electrodeposition products.

The results of XRD and Raman spectroscopy analyses have also illustrated the complex phase composition and chemical structure of the anode mud (Fig. 15g–j). The phase compositions generated using the two power sources are predominantly MnO₂, Mn₂O₃, Mn₃O₄ and SeO₂^{64–68}.

The XPS survey scan of the anode mud has identified the principal elemental composition as Mn, O, N, S, and Pb (Fig. 15k, l). The distribution of these elements is shown as a function of time in Fig. 15m. The XPS spectrum for O1s was subjected to a peak fitting procedure⁶⁷. The results have indicated that the surface oxygen content of anode mud generated by CC is higher than the DC electrolysis by-products. Furthermore, the surface oxygen content exhibited a declining trend over time. The complexity of the anode mud poses serious challenges in terms of accurately quantifying physical composition while ensuring experimental reproducibility.

Discussion

The electrodeposition of manganese metal is a complex kinetic system involving a number of interrelated variables, including time, space, energy, electrochemical reactions and ion migration in the flow field. The spatial variables are primarily reflected in the apparent morphology of the manganese metal. Energy is the most significant variable in this study, where we have considered the replacement of a conventional power source with a continuous, uniform input of electrical energy and continuous variable-speed supply. The electrochemical reactions that occur during the electrodeposition of manganese metal are primarily crystallization reactions at the electrode plate interface. The resulting concentration changes are a consequence of these reactions. Ion migration involves the directional migration of ions in solution during the energization process. It can be demonstrated that CC effectively regulates the kinetic behavior of the manganese metal electrodeposition process (Fig. 16). The findings of this study support the following three observations.

1. The time-varying currents, which include chaos-a, chaos-b, period 1, and period 2, can impede the electrochemical oscillation behavior.
2. The size of manganese nodules increases with the duration of electrodeposition by DC, demonstrating a clear spatial variation in the electrodeposition process. Application of CC promotes energy saving in the initial stages (30 min) of electrodeposition.
3. The occurrence of nodules results in a reduction in current efficiency and increased energy consumption. Increasing the thickness of the deposited manganese metal reduces the energy consumption associated with the time-varying current. Operation of CC at the optimal current density (1270 A/m² (0.508 A)) can improve current efficiency by 6.08%. Nodules are not produced during DC or CC electrolysis when the current density is too low. However, the introduction of high external energies can result in a destabilization of the kinetic system, which in turn impedes the suppression of manganese nodules, even in the presence of time-varying currents^{39,40}.

The primary reasons for enhanced energy saving and emission reduction associated with Mn metal electrodeposition using a chaotic power supply can be attributed to the following factors: (1) The distribution of input energy across the electrode plate is more uniform, circumventing the build-up of electrons at the edge for an extended period; (2) The regulation of electrical energy input controls the electrochemical reaction at the interface of the electrode plate, which alters the migration and transformation of the Mn²⁺ ions in the electrolytic cell.

Conclusions

Previous studies on the electrodeposition of manganese metal by CC have noted that the effects of waveform structure and electrodeposition time on current efficiency warrant further investigation. The main conclusions of this study are as follows:

- (1) A novel methodology for constructing an offset boosting function for any chaotic systems was proposed. Through the synergistic integration of this proposed approach with traditional offset boosting, a novel four-dimensional chaotic system, equipped with two-dimensional offset boosting capabilities, was successfully developed. In addition, this 4D chaotic system was successfully transferred to a real chaotic circuit and was used for in the manganese metal electrolysis system, supplanting conventional DC. The amplitude and waveform of the voltage for the chaotic circuit were established. In addition, a two-dimensional offset boosting function was implemented, which can be employed to control the amount of current while expanding the range of applications for electrical signals. The chaotic circuit comprises a single nonlinear term (a single multiplier) that further reduces the cost of implementation.
- (2) An effective coupling of electrical energy and chemical reactions was achieved through the use of time-varying current, which resulted in the complete suppression of electrochemical oscillations. All four types of waveforms (period 1, period 2, chaos-a, and chaos-b) have been demonstrated to fully inhibit electrochemical oscillations of manganese metal. The ratio of voltage to current indicates that the time-varying current electrodeposition can reduce the cell voltage, achieving energy savings compared with DC. The extent of the reduction in cell voltage from a high to a low level is as follows: chaos-a > chaos-b > period 2 > period 1.

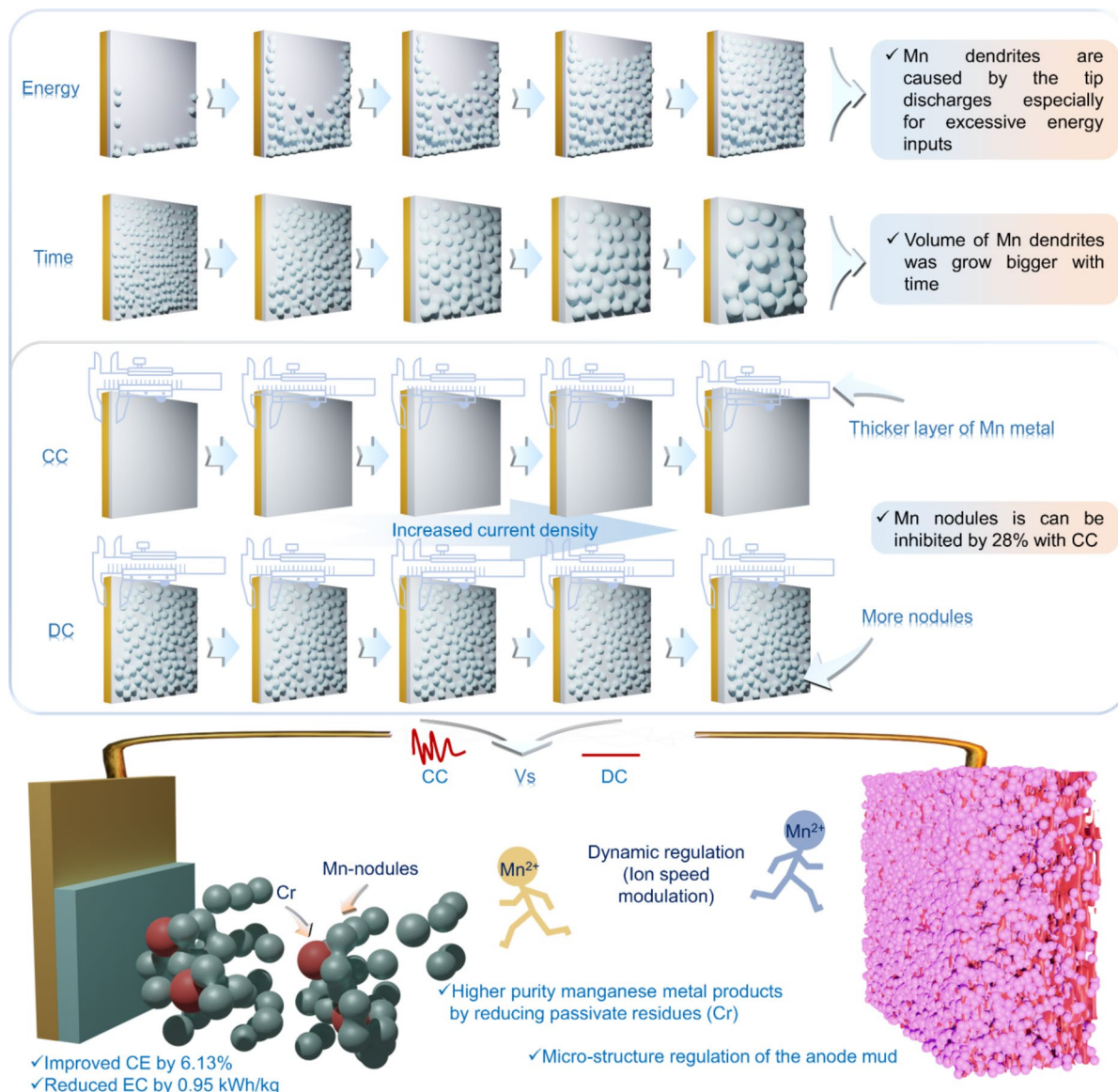


Fig. 16. Schematic representation of the manganese metal deposition mechanism.

- (3) Both the amplitude fluctuation and the waveforms can influence current efficiency. The thickness of the deposited manganese metal can be enhanced, thereby reducing the energy consumption associated with the time-varying current. Moreover, the CC has an optimal current density at 1270 A/m² (0.508 A), which can improve current efficiency by 6.08%. Furthermore, the chaos-a current can increase the current efficiency by 5.83% and with an energy consumption saving of 0.58 kWh/kg for an electrodeposition time of 30 min, which is associated with the largest current fluctuation range.
- (4) Current efficiency decreased with increasing electrodeposition time. Furthermore, the current efficiency can be increased by 6.13%, the area ratio of the manganese nodules reduced by 28%, and the energy consumption reduced by 0.95 kWh/kg compared with DC when the electrodeposition time is 30 min.

This study offers new insights and results related to the use of time-varying currents to deliver an efficient electrodeposition process applied to manganese metal. Nevertheless, the frequency effects of the electrical signals in the electrodeposition process, and the industrial amplification challenges of CC with associated cost considerations, are of critical importance in future research.

Data availability

All data generated or analysed during this study are included in this published article and its supplementary information files.

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Author contributions

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

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