Study on the effects of temperature, deposition cycle number, and cobalt additives on the properties of the positive active material in nickel-cadmium batteries

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Received 19 May 2025; Revised 10 Jul. 2025; Accepted 20 Sep. 2025; Published 2 Oct. 2025.
DOI: https://doi.org/10.54939/1859-1043.j.mst.106.2025.87-93

ABSTRACT

This study investigates the effects of deposition temperature, number of deposition cycles, and cobalt (Co) additives on the structural and electrochemical properties of the positive active material in nickel–cadmium (Ni–Cd) batteries. The purpose is to optimize fabrication parameters to enhance material utilization efficiency and battery performance. Electrodes were fabricated by impregnating porous nickel substrates with nickel nitrate solution, followed by chemical conversion in potassium hydroxide under varying temperatures (65 – 80 °C) and repeated for different cycle numbers (1 – 5). A cobalt nitrate post-treatment was applied to selected samples. Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), and hydrostatic weighing methods were employed to characterize microstructure, composition, density, and porosity. Charge–discharge performance was evaluated using prototype Ni–Cd cells. Results show that the optimal deposition temperature range is 70 – 75 °C, which promotes uniform active material distribution and high density while maintaining sufficient porosity. Four deposition cycles yielded the best balance between mass loading and structural stability. The addition of cobalt improved utilization efficiency by approximately 5.2% and reduced internal resistance from 7.15 mΩ to 4.85 mΩ. These findings provide a scientific basis for improving Ni–Cd electrode fabrication, and future studies may explore long-term cycling behavior and alternative conductive additives.

Keywords: Nickel–cadmium (Ni–Cd) batteries; Cobalt (Co) additives; Deposition temperature; Deposition cycles.

1. INTRODUCTION

Nickel-Cadmium (Ni-Cd) batteries have been widely utilized in various applications due to their robust performance, long cycle life, and high reliability. The electrochemical behavior and durability of these batteries are primarily determined by the properties of their electrode materials, particularly the positive active material composed mainly of nickel hydroxide ($Ni(OH)_2$) [1].

Improving the performance of Ni-Cd batteries requires a detailed understanding of the factors that affect the formation and behavior of the cathode material. Among the most influential factors are the synthesis temperature, the number of deposition cycles used during electrode preparation, and the incorporation of cobalt (Co) as a dopant [2-4]. Each of these parameters can significantly alter the microstructure, phase stability, and electrochemical characteristics of the resulting material [5].

In particular, cobalt additives have been widely studied for their ability to enhance the electrical conductivity, redox reversibility, and structural stability of nickel hydroxide-based active materials. Cobalt can facilitate the stabilization of the γ-NiOOH phase during charge-discharge processes, reduce polarization, and improve high-rate performance and cycle life [6, 7]. Recent studies have also demonstrated that Co-doped electrodes exhibit more compact microstructures, improved mechanical adherence, and superior electrochemical utilization compared to undoped counterparts [8, 9]. Co^{2+} ions partially substitute Ni^{2+} in the brucite-like lattice, improving structural stability, reducing lattice strain during cycling, and enhancing the reversibility of redox reactions.

Despite the long-standing use of Ni-Cd batteries, there is renewed interest in optimizing their electrode performance, particularly for specialized applications such as aerospace, military-grade electronics, and standby power systems where thermal stability, longevity, and reliability are paramount [10, 11]. Furthermore, enhancing material utilization efficiency and reducing internal resistance remain critical to minimizing material costs and extending battery lifespan, thus underscoring the urgency of investigating key fabrication parameters.

This study addresses the need to improve Ni-Cd battery electrodes by systematically analyzing how temperature, deposition cycle number, and cobalt doping influence the microstructural and electrochemical behavior of the positive active material. The outcomes aim to provide design guidance for durable and efficient Ni-Cd battery systems applicable in high-demand environments.

2. EXPERIENCE

2.1. Fabrication of positive electrodes

Positive electrode collectors were prepared by cutting 99.9% pure perforated nickel sheets into 1×1 cm squares. These were impregnated with nickel nitrate (specific gravity 1.65 ± 0.01 g/cm³) at 75 ± 5 °C for 2 hours, followed by air drying. Samples were then soaked in KOH solution (1.20 ± 0.01 g/cm³) at 60–80 °C for 1 hour, rinsed, and dried.

For cobalt treatment, electrodes were immersed in cobalt nitrate (1.35–1.40 g/cm³) at 18–30 °C for 1 hour, air-exposed for 2 hours, then treated with KOH under the same conditions.

To study temperature effects, the KOH soaking step was varied at 65, 70, 75, and 80 °C [12]. The impact of deposition cycles was assessed by repeating this process for multiple cycles.

2.2. Fabrication of prototype Ni-Cd batteries

Test batteries (6 Ah theoretical capacity) were assembled using six positive plates prepared under optimal temperature and cycle conditions, with and without cobalt treatment.

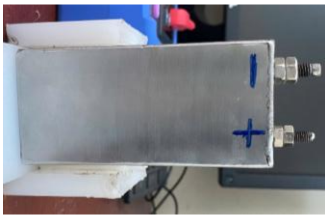

***Figure 1**. Prototype Ni-Cd battery after assembly.*

Negative plates (6 Ah) were made from a paste of 98% CdO and 1% CMC with nickel powder, applied to perforated nickel sheets, then dried and wrapped in 0.015 mm polyester separators. Each battery included seven negative plates to ensure excess capacity for accurate evaluation of positive electrode performance. The electrolyte was a KOH solution (specific gravity 1.2 g/cm³).

2.3. Research methods

Used to determine the density and porosity of the porous nickel skeleton [13].

The morphology and elemental composition of the active material were investigated using SEM -EDS, performed with a JSM–IT800 system at the University of Science and Technology of Hanoi.

Electrochemical performance of the prototype batteries was evaluated using a BTS-5V-6A battery tester at the Institute of Chemistry and Materials – Military Science and Technology Institute. The batteries were charged at a constant current of 1 A for 12 hours, followed by discharge at 1 A to a cutoff voltage of 1 V.

3. RESULTS AND DISCUSSION

3.1. Effect of deposition temperature on the properties of the positive electrode active material in nickel-cadmium batteries

Temperature affects both the deposition of nickel salts and their conversion into nickel hydroxide. Deposition was conducted on porous nickel substrates at 75 °C, followed by treatment with potassium hydroxide (specific gravity 1.2) at 65–80 °C to induce precipitation. After drying, electrode parameters were measured (table 1).

Results show that at 65–70 °C, thickness increased by 4–5 µm and mass by ~25%. At 75 °C, the thickness reached 7 µm with similar mass gain. However, at 80 °C, thickness increased to 10 µm and mass rose to 33%, indicating more rapid and extensive surface reactions..

Table 1. *Technical specifications of electrode samples deposited at various temperatures.*

Parameters		Deposition temperature (°C)			
		65	**70**	**75**	**80**
Thickness (µm)	Initial	318	321	319	318
	After Deposition	322	326	326	329
Mass (g)	Initial	0,030	0,030	0,031	0,030
	After Deposition	0,037	0,038	0,038	0,040
Density (g/cm³)	Initial	5,42	5,45	5,41	5,42
	After Deposition	6,15	6,19	6,23	5,82
Porosity (%)	Initial	69,9	71,8	70,1	72,5
	After Deposition	34,6	32,4	31,1	22,2

Despite limited thickness increases at lower temperatures, sample density rose and porosity remained above 30%, suggesting capacity for further deposition. In contrast, at 80 °C, although mass gain was highest, density decreased, and porosity dropped to ~20%. This indicates that rapid surface precipitation forms a dense outer layer, hindering deeper penetration and leaving the inner structure underutilized. To better understand the relationship between salt concentration and structural changes, SEM imaging was performed to examine the material morphology and internal transformations within the electrode (figure 2).

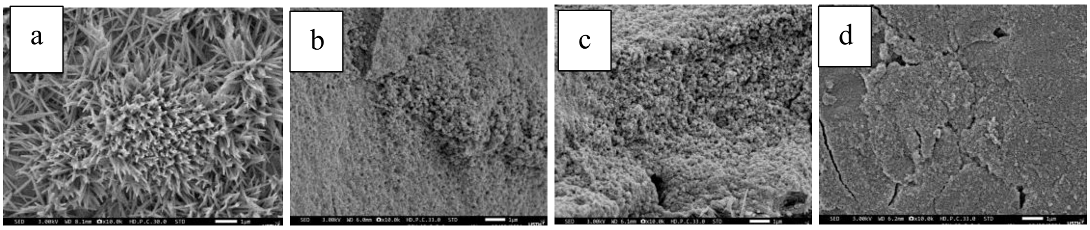

Figure 2. *SEM images of positive electrode samples deposited at different temperatures: a) 65 °C; b) 70 °C; c) 75 °C; d) 80 °C.*

SEM analysis reveals that temperature affects not only the reaction rate but also the morphology of the active material. At 65 °C, although macro-parameter changes were similar to those at 70 and 75 °C, the resulting microstructure differed significantly. Needle-like crystals measuring 2–3 µm in length were observed. This morphology imparts porosity but results in lower electrochemical conversion efficiency.

At 70–75 °C, spherical particles (~100 nm) were uniformly deposited both inside and on the electrode surface. In this temperature range, solution diffusion precedes precipitation, enabling efficient impregnation and uniform reaction throughout the electrode bulk. As a result, although mass increased, thickness remained nearly constant, and material density improved.

At 80 °C, the spherical morphology was lost, replaced by dense surface agglomerates. Rapid precipitation occurred immediately upon contact with the alkaline solution, forming a surface layer that hindered further diffusion. Consequently, mass and thickness increased, but density and porosity significantly decreased.

Thus, the combined results indicate that the optimal temperature range for both impregnation and precipitation reactions lies between 70 °C and 75 °C.

3.2. Effect of deposition cycle number on the properties of the positive electrode active material in nickel-cadmium batteries

The deposition process typically requires multiple cycles to achieve the target quantity of active material on the electrode or to reach the calculated theoretical amount. To monitor and control this process, depositions were performed on porous nickel substrates using nickel salt solutions. A potassium hydroxide (KOH) solution with a specific gravity of 1.2 was used to precipitate the deposited salts, applied over 1 to 5 deposition cycles. After drying, the electrodes were analyzed for their physical and structural parameters. The results are presented in figure 3 and figure 4.

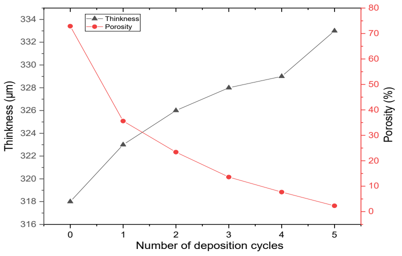

Figure 3. *Dependence of electrode thickness and porosity on the number of deposition cycles.*

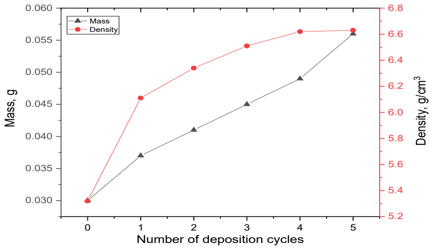

Figure 4. *Dependence of electrode mass and density on the number of deposition cycles.*

The graphs indicate that electrode thickness increases with the number of deposition cycles. The slope of the thickness increase declines over the first four cycles, but a sudden jump is observed at the fifth cycle (figure 3). Generally, increasing thickness correlates with increases in mass and density. Figure 4 shows that this trend holds for the first four cycles: mass gain is most significant in the first cycle due to high porosity, then decreases gradually through cycles 2 to 4. However, at the fifth cycle, both mass and thickness rise sharply.

Interestingly, this trend does not continue for electrode density. While density increases gradually over the first four cycles, this progression halts at the fifth cycle. The most likely explanation is that during early cycles, porous voids are gradually filled with deposited active material, thereby increasing density. By the fifth cycle, the voids are no longer being filled effectively—instead, excess material is deposited predominantly on the outer surface, blocking pore access and resulting in an apparent increase in volume without further compaction of the internal structure. This interpretation is supported by figure 3, which shows a sharp drop in porosity at the fifth cycle. Despite this drop, the density remains unchanged, suggesting that additional mass is not contributing to internal densification but rather forming a loose surface layer.

To assess microstructural changes with deposition cycles, SEM analysis was performed (figure 5). From the first to the fourth cycle, spherical particles (~ 100 nm) were observed, becoming progressively denser with reduced porosity. By the fourth cycle, pores were nearly closed, and particle boundaries began to merge. In the fifth cycle, the spherical morphology disappeared, forming a dense, continuous layer that blocked the pores.

This transition indicates that after four cycles, the active material reaches optimal deposition within the structure. Further cycles lead to surface-layer buildup, which is mechanically unstable and prone to delamination during handling or operation.

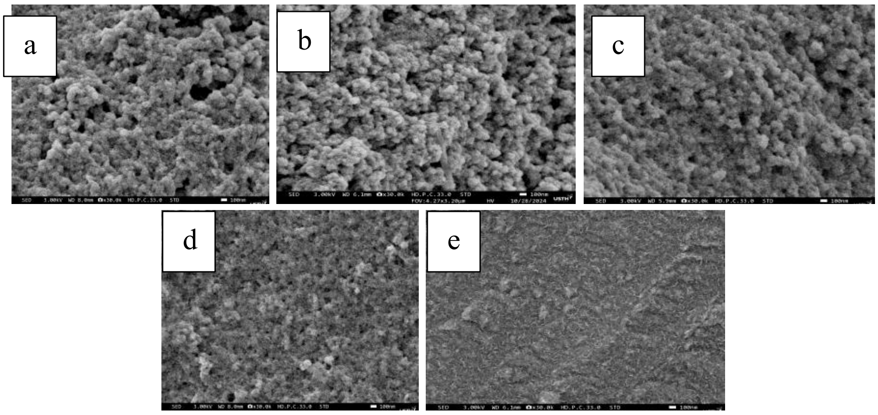

Figure 5. SEM images of positive electrode materials after different numbers of deposition cycles: a – 1 cycle; b – 2 cycles; c – 3 cycles; d – 4 cycles; e – 5 cycles.

3.3. Effect of cobalt additives on the utilization efficiency of the positive electrode

Cobalt was introduced to improve the electrode's electrical conductivity. Uniform cobalt distribution is critical to prevent localized current buildup and elevated internal resistance. To evaluate this, EDS mapping and XRD analysis were performed. As shown in figure 6, Ni, Co, and O were uniformly distributed, consistent with $Ni(OH)_2$ and $Co(OH)_2$ composition. The even dispersion of cobalt suggests it acts as a conductive bridge between the active material and the nickel substrate.

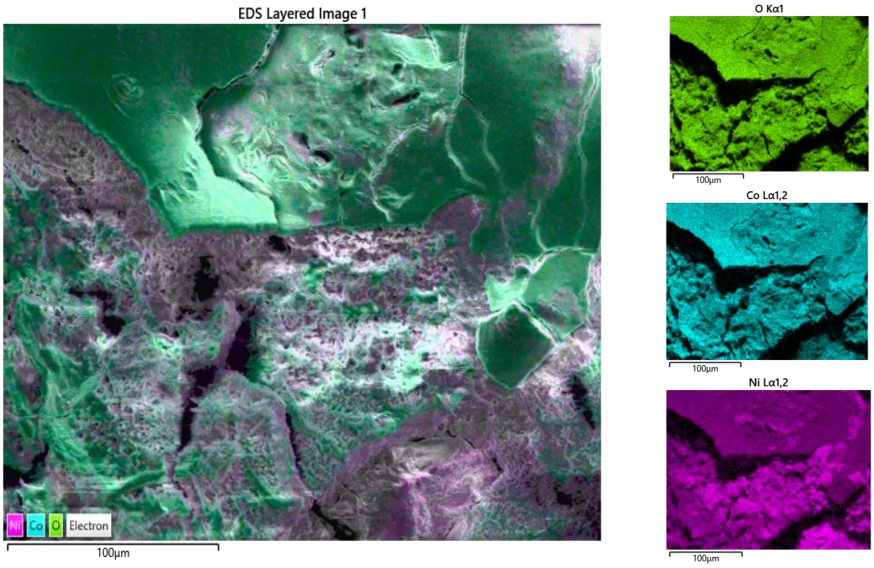

Figure 6. EDS-mapping image of the positive electrode active material after cobalt deposition.

In figure 7, the most intense peak observed at approximately 2θ ≈ 44.5° corresponds to the (111) plane of metallic Ni. The lower-intensity peaks at 2θ ≈ 19° and 33° are assigned to the (001) and (100) planes of β-$Ni(OH)_2$, respectively, confirming the presence of a stable β-phase. The peaks at 2θ ≈ 38° and 51° are consistent with the (111) reflection of metallic Co, while the peak at 2θ ≈ 59° is characteristic of the brucite-type structure. These results suggest a high probability that Co partially substituted Ni within the crystal lattice of β-$Ni(OH)_2$.

The effectiveness of the cobalt additive was evaluated via charge–discharge testing of assembled Ni-Cd cells. Two experimental cells were fabricated, each comprising 14 negative and 13 positive electrode plates. The negative electrodes were designed with excess capacity to ensure that the performance of the positive electrodes could be fully evaluated. The results are summarized in table 2 and illustrated in figure 8.

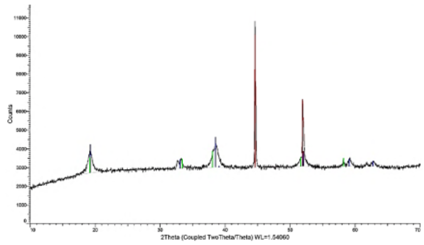

Figure 7. XRD pattern of the electrode sample deposited with cobalt.

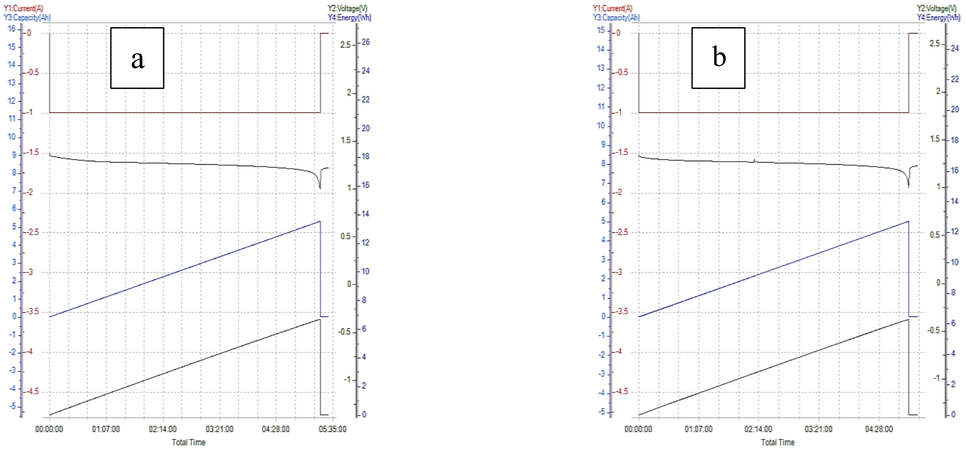

***Figure 8.** Discharge profiles of the Ni-Cd test cells: a – With cobalt; b – Without cobalt.*

***Table 2.** Measured capacity of Ni-Cd test cells.*

	Internal Resistance (mΩ)	No. of Cycles	Theoretical Capacity (Ah)	Measured Capacity (Ah)	Utilization Efficiency (%)
Cell 1 (with Co)	4.85	20	6	5.322	88.70
Cell 2 (without Co)	7.15	20	6	5.011	83.51

The cobalt-containing battery achieved a capacity of 5.322 Ah, corresponding to 88.70% utilization efficiency, compared to 5.011 Ah (83.51%) without cobalt. These values remained stable over 20 charge–discharge cycles, confirming the cells' reliability. The ~5.2% improvement suggests cobalt effectively enhances electrode performance.

This improvement is attributed to enhanced charge transfer. Cobalt, as a conductive transition metal, bridges $Ni(OH)_2$ particles to the nickel substrate, forming efficient electronic pathways. This reduces internal resistance (from 7.15 mΩ to 4.85 mΩ) and improves active material utilization. These findings align with previous studies [14] reporting similar benefits from conductive additives.

4. CONCLUSIONS

This study confirms that deposition temperature, cycle number, and cobalt additives critically affect the electrochemical performance of Ni-Cd battery positive electrodes. Optimal results were achieved at 70–75 °C with four deposition cycles, yielding uniform, low-porosity active material. Cobalt addition improved utilization efficiency by ~5.2% and reduced internal resistance by forming conductive pathways between $Ni(OH)_2$ and the nickel substrate. These findings offer a foundation for optimizing Ni-Cd electrode fabrication. Future work should explore long-term cycling, alternative dopants, and process scalability for industrial use.

Acknowledgement: *The authors would like to express their sincere gratitude for the financial support provided by the scientific and technological research project funded by Academy of Military Science and Technology under project code 01/2024/HĐKHCN-HHVL.*

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TÓM TẮT

Nghiên cứu ảnh hưởng của nhiệt độ, số chu kỳ lắng đọng và phụ gia Cobal đến tính chất của chất hoạt động cực dương trong ắc quy Nikel-Cadimi

Trong nghiên cứu này đánh giá ảnh hưởng của nhiệt độ lắng đọng, số chu kỳ lắng đọng và phụ gia cobalt (Co) đến cấu trúc và tính chất điện hóa của chất hoạt động cực dương trong ắc quy nickel–cadmium (Ni–Cd), từ đó tối ưu hóa quy trình chế tạo nhằm nâng cao hiệu suất sử dụng vật liệu và cải thiện hiệu suất phóng–nạp của ắc quy. Các điện cực được chế tạo bằng cách thấm tẩm dung dịch nitrat niken vào sườn cực niken xốp, sau đó chuyển hóa hóa học trong dung dịch kali hydroxit ở các mức nhiệt độ khác nhau (65–80 °C) và thực hiện với số chu kỳ lặp lại từ 1 đến 5. Một số mẫu được xử lý bổ sung bằng dung dịch nitrat cobalt. Cấu trúc vi mô và thành phần được phân tích bằng phương pháp hiển vi điện tử quét (SEM) và phổ tán xạ tia X (EDS). Khối lượng riêng và độ xốp được xác định bằng phương pháp cân thủy tĩnh. Tính năng phóng–nạp được đánh giá thông qua các ắc quy mẫu thử nghiệm. Kết quả cho thấy vùng nhiệt độ tối ưu là 70–75 °C, giúp vật liệu phân bố đồng đều, mật độ cao và vẫn duy trì độ xốp phù hợp. Số chu kỳ lắng đọng tối ưu là 4 chu kỳ. Việc bổ sung cobalt giúp nâng hiệu suất sử dụng vật liệu lên khoảng 5.2% và giảm nội trở từ 7,15 mΩ xuống còn 4,85 mΩ. Những kết quả này cung cấp cơ sở khoa học cho việc cải tiến quy trình chế tạo điện cực ắc quy Ni–Cd. Nghiên cứu tiếp theo có thể mở rộng theo hướng khảo sát độ bền chu kỳ dài và thử nghiệm các phụ gia dẫn điện khác.

Từ khoá: Ắc quy Ni-Cd; Phụ gia Coban; Nhiệt độ lắng đọng; Chu kỳ lắng đọng.