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ORIGINAL ARTICLE

Adhesion and Stability Increased Carbon Nanowall for the Application to Lithium-Ion Batteries

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Abstract

Carbon nanowalls are used as electrodes for second batteries because of the widest reaction surface area among the carbon-based nanomaterials, but their practical application is limited due to the disadvantages of adhesion and stability to lithium-ion batteries. In this research, titanium, titanium nitride, and chromium layers were used as an interlayer between the copper foil and the carbon nanowalls in order to increase the adhesive force and stability. The interlayer was deposited on the substrate using a radio frequency (RF) magnetron sputtering system with a four-inch Ti, TiN, or Cr target. The carbon nanowalls are then grown on interlayer-coated copper foil using a plasma-enhanced chemical vapor deposition (PECVD) system and used as a charge collector for lithium-ion batteries. The middle layer of each sample was identified using a field emission scanning electron microscope (FE-SEM). Impedance measurement and charge/discharge tests were performed to evaluate the characteristics of a lithium-ion battery. Based on the results of this experiment, it was noticed that the research goal can be achieved by inserting the mentioned intermediate layers, and CNWs synthesized on TiN interlayers present the best capacity retention measurement results, which is critical for the future development of lithium-ion batteries.

Keywords Anode material · Adhesion · Carbon nanowall · Energy storage · Stability

1 Introduction

Nowadays, as the result of increasing energy demand in various industries promoting the development of energy storage and power conversion systems, many studies on the growth of high-efficiency energy storage equipment such as secondary batteries and supercapacitors are currently being done [1–3]. Lithium-ion batteries (LIBs) have been successfully employed in various industries and have become one of the essential elements in the current period due to their lightweight, great energy storage, conversion capacity, and high-efficiency energy with high energy density [4–8]. Today, there are 7.19 billion active mobile phones [9], nearly 1 billion laptop computers, and another billion tablets on the planet [10]. This demand for LIBs from the consumer electronics sector will not only stay high but will also rise because of the increasingly relevant idea of energetic transition which will lead to a shift in the automobile industry from fossil fuel-based mobility to electric vehicles (EVs) [11].

A considerable improvement in the anode material of a battery can result in benefits in a variety of basic battery performance issues, such as cost, adaptability, safety, reliability, capability, cycle life, and temperature impacts [12]. Numerous previous studies confirmed that graphite is one of the most significant minerals for anode material in batteries [2]. Graphite anode materials are used in a broad range of lithium-ion battery manufacturing settings, from research laboratories to commercial production plants. They keep electrical contact between the active material particles and the current collector. In addition, thanks to their high electrical conductivity and large surface area, they decrease the electrode polarization potential and improve the cycle life of the battery [13–15]. Many innovative materials for the next generation of LIBs have been investigated, particularly high-performance anode materials [16]. Alloys, conversion-type transition metal compounds, silicon-based compounds, and carbon-based compounds are among them [17]. In recent times, graphene materials have emerged as one of the most promising alternatives for LIB anodes because of their high theoretical specific capacity (744 mAh/g), huge

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specific surface area, superior electrical conductivity, and efficient carrier mobility, and broad electrochemical window. Carbon-based nanomaterials attracted great at tention from researchers and one of them was CNT, which was used because of being more capable of storing and converting energy than standard graphite electrodes [18].

Remarkably, small adjustments to some synthesis procedures result in the formation of carbon nanowalls (CNWs) or carbon nanorods instead of carbon nanotubes. The morphology of the carbon layer under certain techniques depends largely on the pressure and gas flow rate as shown and this research is to use a plasma-enhanced chemical vapor deposition (PECVD) system at average pressure and gas flow rate, therefore, CNWs were formed. Carbon nanowalls contain a vertically grown graphene structure and have the benefit of high electrical conductivity, the rapidly diffusing electrons and electrolytes due to their enormous graphene surface area rather than carbon nanotubes [19–23]. Furthermore, the data reveal that the CNW has a very small mass, which has the advantage of allowing more lithium-ions to be stored in the small mass [18]. However, low adhesion to the substrate is one of the most important issues that are usually encountered in the application of CNWs. It is a popular practice to enhance the adhesion strength of a coating on a substrate by adding a pure metal interlayer such as Ti or Cr, the influence of Ti and Cr interlayer thickness on residual stress and adhesion strength has been studied extensively while TiN is a typical interlayer with excellent thermal stability and chemical safety, and with high fine hardness [24, 25].

Taking advantages of the interlayer, this work prepared anode active materials that utilize titanium (Ti), titanium nitride (TiN), or chromium (Cr) as an intermediate layer for carbon nanowall that was synthesized to boost the adhesive force and stability. A field emission scanning electron microscope (FE-SEM) cross-sectional image was photographed to identify the middle layer of each sample, and charge/discharge tests and impedance measurements were conducted to evaluate the electrochemical characteristics of lithium-ion batteries to which each anode active material was applied.

2 Experimental Section

2.1 Interlayer Deposition

A copper foil was utilized as a substrate for synthesizing an anode active material of a lithium-ion battery. Before developing a carbon nanowall, the copper foil was separately cleaned in trichloroethylene (TCE), acetone, methanol, and distilled water for 10 min, respectively. The oxide formed on the surface of copper foil as a result of contact with the air was removed by washing with dilute foil. Subsequently, nitrogen gas was used to dry the copper foil. The cleaned wafer was coated with immediate layers using an RF magnetron sputtering system and four-inch metal targets (Ti, TiN, or Cr). Argon (Ar) gas was injected as the sputtering gas, and the working pressure was maintained at 1.5×10^{-4} Torr. The Ti and TiN targets were sputtered for 15 min while the Cr target was sputtered for 10 min at 300 W RF power, and each was attached to a substrate via spinning at 1700 rph during deposition.

2.2 Carbon Nanowall Growth

For the synthesis of the CNWs, a plasma-enhanced chemical vapor deposition (PECVD) was used. A base pressure of 1×10^{-5} Torr was maintained in the PECVD chamber, and methane (CH_4) gas and hydrogen (H_2) gas were injected into the chamber in a ratio of 2:1. In this stage, the working pressure in the chamber was kept at 4×10^{-1} Torr, and the CNWs were synthesized at 700 °C for 15 min. After the growth was completed, the wafer was slowly cooled to room temperature, and then the CNWs grown on interlayer-coated substrates were taken out of the chamber (Fig. 1).

The types and properties of the CNWs on interlayer-coated copper foil were studied using field emission scanning electron microscopy (FE-SEM, Hitachi S-4800, Krefeld, Germany). Impedance measurements and charge/discharge tests were also carried out to analyze the characteristics of a lithium-ion battery with three intermediate layers applied to a carbon nanowall. The detailed experiment conditions are summarized in Tables 1 and 2.

3 Results and Discussion

3.1 Structural Characteristic

FE-SEM was used to investigate the CNWs synthesized on interlayers by sputtering and chemical vapor deposition. The results are presented in Fig. 2 the growth of carbon nanowalls on the intermediate layer of each sample was well performed. The heights of the CNWs were nearly similar between the Ti layer and the TiN layer. However, Fig. 2a reveals that a Ti intermediate layer was inserted between the CNW and the copper foil shows low adhesion to the substrate, the reason for this is that when Ti is exposed to the atmosphere, it is oxidized to TiO_2 [25], which reduces the homogeneity of the substrate utilized for CNW formation. This leads to the walls to quickly break down at very low stresses, causing the substrate and CNW to be separated [22]. For this reason, when CNWs grown on Ti interlayer were utilized for anode materials, they would have an adverse influence on adhesion and stability to lithium-ion batteries. The CNW on the TiN layer, on the other hand, was found to have better adhesion because the TiN

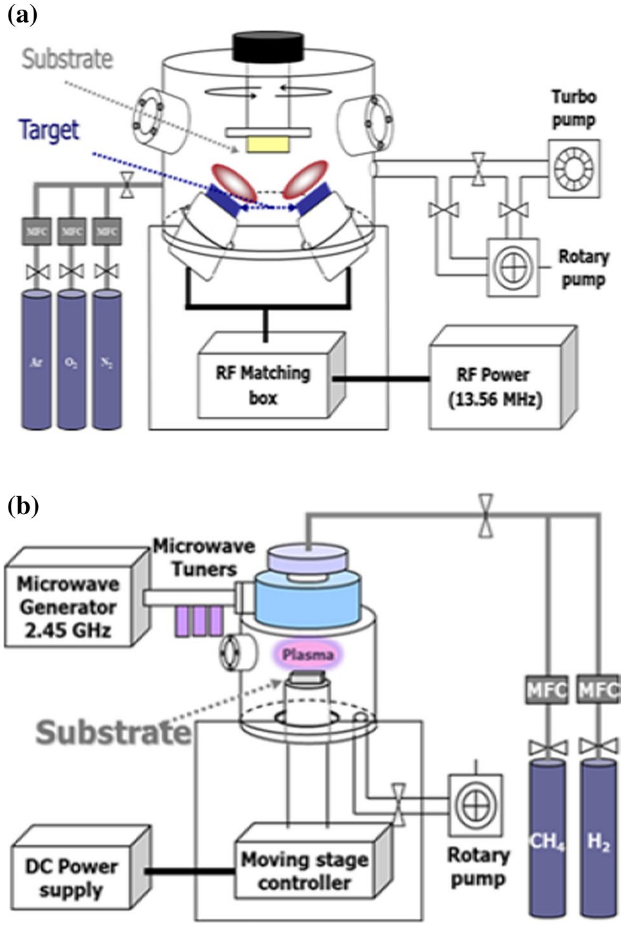

Fig. 1 Schematic of the processing equipment used in this experiment; **a** RF magnetron sputtering system, **b** microwave PECVD system

Table 1 Deposition conditions of the interlayers by the RF magnetron sputtering system

	Ti layer	TiN layer	Cr layer
Substrate	Copper foil		
RF power	300 W		
Target	Ti	TiN	Cr
Working pressure	15 mTorr		
Substrate temperature	Room temperature		
Deposition time	15 min	15 min	10 min

interlayer containing a small amount of Ti_3O has a rougher surface than the etched Ti substrate, resulting in a significant increase in the bonding strength of the coated electrode which appears to be consistent with the research expectations [26]. Despite the fact that the deposition time was the shortest of the three targets employed, only the thickness of the Cr interlayer was evident.

Table 2 Growth Conditions of the CNWs by the microwave PECVD system

Parameters	Conditions
Substrate	Copper foil
Reaction gas	H_2, CH_4
Working pressure	40 mTorr
Substrate temperature	700 °C
Growth time	15 min

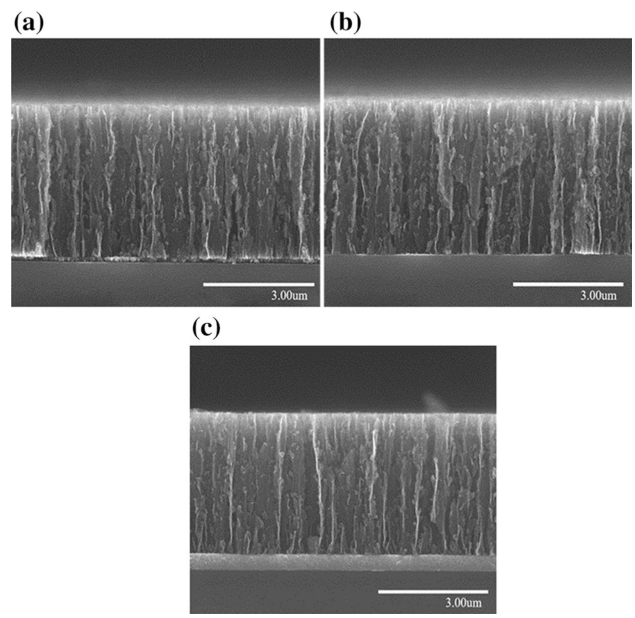

Fig. 2 Cross-sectional images of carbon nanowalls grown on the metal interlayer; **a** Ti layer, **b** TiN layer, **c** Cr layer

The enhancement of adhesion strength of the coating by using interlayer was investigated both their thickness and influence levels. The results of the cross-sectional image analysis of carbon nanowalls grown on Ti, TiN, and Cr layers demonstrate that adding a Ti interlayer improves adhesion strength more insignificantly than TiN and Cr interlayers. Furthermore, TiN interlayers, rather than Cr interlayers, have an optimum interlayer thickness for adhesion strength.

3.2 Impedance Measurement

For the coin cell's Electrochemical Properties Evaluation, each sample was established as an anode active material with impedance measurements. The resistance between the values can be evaluated by measuring the impedance of the collector (copper foil) and the negative electrical charge flowing through the active material (middle layer and carbon nanowall).

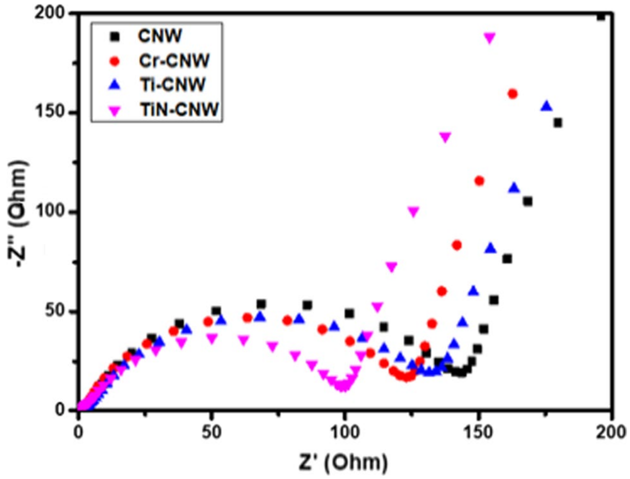

Fig. 3 Impedance measurement results of coin cells manufactured using each sample as an anode active material

The diameter of the semicircle in the coin cell's impedance graph represents the resistance between the charge collector (copper foil) and the anode active material (intermediate layer and carbon nanowall). For the Ti and Cr layers, where CNWs were synthesized, the impedance values were very high at 129 Ohms and 122 Ohms, respectively while the TiN sample has the smallest resistance value at 97 Ohms. This can be explained by the fact that TiN is a high-strength ceramic-like substance with excellent electrical conductivity and corrosion resistance [26]. Based on the survey results, a CNW/TiN/copper foil anode containing the TiN interlayer should present a promising future for secondary batteries with high stability and electrical conductivity performance (Fig. 3).

For evaluation of the electrochemical properties of the coin cell manufactured using each sample as the anode active material, the capacity retention rate was measured through a charge/discharge tester. The test objective is to determine the number of times a lithium-ion battery can be used by evaluating it until it deteriorates after repeated cycles of charging and discharging as well as calculate how much charge capacity is maintained as the coin cell continues its charge and discharge cycle. Based on Fig. 4a, b, and c the discharge capacity of all materials was found to be decreased with increasing charge/discharge cycle. As a result of measuring up to 100 cycles of coin cells produced using each sample as the anode active material, the sample using the TiN intermediate layer exhibited the highest capacity retention rates. Therefore, it is vital to consider the TiN layer as a promising material for enhancing stability for application to lithium-ion batteries.

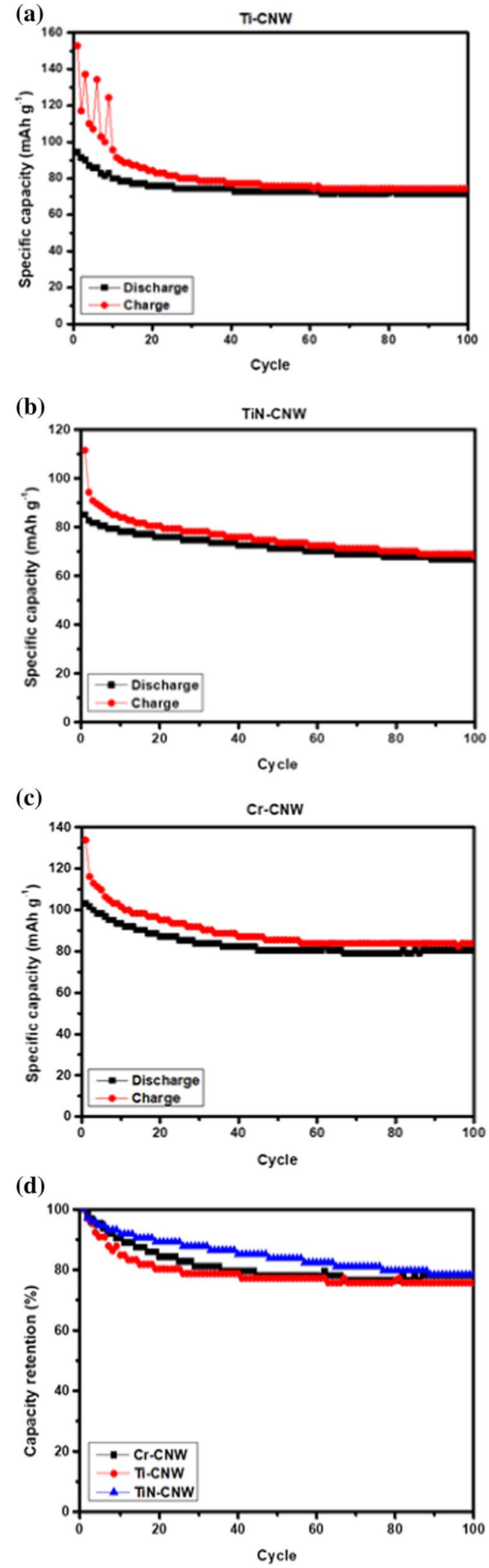

Fig. 4 Charge/discharge test results of lithium-ion batteries made with each sample; **a** Ti-CNW, **b** TiN-CNW, **c** Cr-CNW, **d** capacity retention for each sample

4 Conclusions

This present study focused on a specific aspect of LIB design, namely, enhanced LIB anode materials. The CNWs were synthesized on interlayer-coated copper foil in order to increase the utilization of CNWs for lithium-ion batteries. The cleaned substrate was coated with thin layers using four-inch metal targets (Ti, TiN, or Cr) and an RF magnetron sputtering system. With the use of a plasma-enhanced chemical vapor deposition (PECVD), CNWs were synthesized on the interlayers using CH_4 and H_2 as the reaction gases. The middle layer of each sample was identified using an FE-SEM cross-sectional image; the results show that the formation of carbon nanowalls on each sample of the intermediate layer was exceptional.

The critical difficulties concerning the adhesive force and durability of carbon nanowalls as an anode active material can be addressed by depositing one of the Ti, TiN, or Cr layers as an interlayer between the copper foil and the carbon nanowalls. The adherence improvement of the CNW on the TiN and Cr layers was supposed to be more effective than that of the Ti substrate but the high thickness of the Cr layer appears to be inappropriate for anode metrical for lithium-ion batteries. This study also revealed that the appropriate properties of the interlayer mentioned have a considerable impact on the life extension of the anode. The impedance values for the Ti and Cr layers, where CNWs were synthesized, were relatively high whereas the TiN sample has the minimum resistance value.

In conclusion, our research suggests that TiN is the most effective material for increasing structural stability, resulting in improved anode electrochemical performance. These results have also inspired interest in the development of additional rechargeable lithium-ion batteries.

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References

1. Steele BC, Heinzel A (2001) Materials for fuel-cell technologies. Nature 414(6861):345–352
2. Rui X, Geng Y, Zhuang M, Xiao S, Sun X (2022) Emergy-based environmental accounting of graphite anode material production. J Clean Prod 339:130705
3. Lee S, Choi WS, Yoo J, Lim DG, Kim HJ, Lee HJ, Hong B (2014) Fabrication of metal-coated carbon nanowalls synthesized by microwave plasma enhanced chemical vapor deposition. J Nanosci Nanotechnol 14(12):9189–9193
4. Yang Y, Han Y, Jiang W, Zhang Y, Xu Y, Ahmed AM (2021) Application of the supercapacitor for energy storage in China: role and strategy. Appl Sci 12(1):354
5. Mohamad F, Teh J, Lai CM, Chen LR (2018) Development of energy storage systems for power network reliability: a review. Energies 11(9):2278
6. Masias A, Marcicki J, Paxton WA (2021) Opportunities and challenges of lithium ion batteries in automotive applications. ACS Energy Lett 6(2):621–630
7. Huang S, Zhu X, Sarkar S, Zhao Y (2019) Challenges and opportunities for supercapacitors. APL Mater 7(10):100901
8. Blomgren GE (2016) The development and future of lithium ion batteries. J Electrochem Soc 164(1):A5019–A5025
9. Goyal MR, Eilu E (2019) Digital media and wireless communications in developing nations: agriculture, education, and the economic sector. CRC Press, Florida
10. Akcil A (2019) Critical and rare earth elements: recovery from secondary resources. CRC Press, Florida
11. Brown LR (2015) The great transition: shifting from fossil fuels to solar and wind energy. WW Norton & Company, New York
12. Yen J-P, Chang C-C, Lin Y-R, Shen S-T, Hong J-L (2014) Sputtered copper coating on silicon/graphite composite anode for lithium ion batteries. J Alloy Compd 598:184–190
13. Wang S, Liu D, Cai X, Zhang L, Liu Y, Qin X, Zhao R, Zeng X, Han C, Zhan C, Kang F (2021) Promoting the reversibility of lithium ion/lithium metal hybrid graphite anode by regulating solid electrolyte interface. Nano Energy 90:106510
14. Kriegler J, Hille L, Stock S, Kraft L, Hagemeister J, Habedank JB, Jossen A, Zaeh MF (2021) Enhanced performance and lifetime of lithium-ion batteries by laser structuring of graphite anodes. Appl Energy 303:117693
15. Engels P, Cerdas F, Dettmer T, Frey C, Hentschel J, Herrmann C, Mirfabrikikar T, Schueler M (2022) Life cycle assessment of natural graphite production for lithium-ion battery anodes based on industrial primary data. J Clean Prod 336:130474
16. Nzereogu PU, Omah AD, Ezema FI, Iwuoha EI, Nwanya AC (2022) Anode materials for lithium-ion batteries: a review. Appl Surf Sci Adv 9:100233
17. Landi BJ, Ganter MJ, Schauerman CM, Cressand CD, Rachaelle ARP (2008) Lithium-ion capacity of single-wall carbon nanotube paper electrodes. J Phys Chem C 112(19):7509–7515
18. Lee S, Kwon S, Kim K, Kang H, Ko JM, Choi W (2021) Preparation of carbon nanowall and carbon nanotube for anode material of lithium-ion batteries. Molecules 26:6950
19. Zhu M, Wang J, Holloway BC, Outlaw RA, Zhao X, Hou K, Shutthanandan V, Manos DM (2007) A mechanism for carbon nanosheet formation. Carbon 45(11):2229–2234
20. Zhao J, Shaygan M, Eckert J, Meyyappan M, Rummeli MH (2014) A growth mechanism for free-standing vertical graphene. Nano Lett 14(6):3064–3071
21. Kwon S, Choi H, Lee S, Lee G, Kim Y, Choi W, Kang H (2021) Room temperature gas sensor application of carbon Nanowalls using electrical resistance change by surface adsorption of toxic gases. Mater Res Bull 141:111377
22. Choi H, Kwon S, Kang H, Kim JH, Choi W (2019) Adhesion-increased carbon nanowalls for the electrodes of energy storage systems. Energies 12(24):4759
23. Bo Z, Yang Y, Chen J, Yu K, Yan J, Cen K (2013) Plasma-enhanced chemical vapor deposition synthesis of vertically oriented graphene nanosheets. Nanoscale 5(12):5180–5204
24. Tillmann W, Fehr A, Stangier D, Dildrop M (2019) Influences of substrate pretreatments and Ti/Cr interlayers on the adhesion and hardness of CrAlSiN and TiAlSiN films deposited on Al_2O_3 and ZrO_2-$8Y_2O3$ thermal barrier coatings. Res Phys 12:2206–2212

25. Tran Thi M, Kwon S, Kang H, Kim JH, Yoon YK, Choi W (2022) Growth properties of carbon nanowalls on nickel and titanium interlayers. Molecules 27:406
26. Tang C, Liu Z, Cui D, Yu L, Xue J, Yin X (2021) Enhancing the stability and electrocatalytic activity of Ti-based PbO_2 anodes by introduction of an arc-sprayed TiN interlayer. Electrochim Acta 399:139398

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