



Article Copper-Coated Graphite Felt as Current Collector for Li-Ion Batteries

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Abstract: Lithium-ion batteries (LIBs) undoubtedly are considered a viable option to meet the everincreasing demands for portable consumer electronic devices and electric vehicles. To meet this requirement, intensive research is being conducted on increasing the volumetric and gravimetric energy density of LIBs as well as developing high-capacity electrode materials for LIB. In this study, a novel copper-coated graphite felt as a current collector is proposed for use as a constituent of LIB. Different type of Cu-coated graphite felt electrodes were synthesized. They were characterized by X-ray Diffractometer (XRD). To test its electrochemical performance Electrochemical Impedance Spectroscopy (EIS) and cyclic voltammetry (CVA) techniques were used. Materials with a specific capacity of up to 473 mAh \cdot g⁻¹ were obtained. It was found that the nature of the capacity gain of carbon felt electrodes differs from that of graphite due to a different crystal structure. The use of a copper coating reduces the charge transfer resistance and increases the capacity of the material. Therefore, such new type of anode materials may be successfully used in LIBs.

Keywords: lithium-ion battery; graphite felt; electrochemical deposition; current collector

1. Introduction

Among the different types of rechargeable batteries (e.g., nickel–cadmium, nickel– metal hydride, and lead-acid), Li-ion batteries (LIBs) have made significant progress since their first commercial implementation in June 1991 [1] by Sony Corporation. Nowadays, LIBs prevail in the worldwide battery market of consumer electronic devices and have been widely recognized as an ideal flexible energy storage medium [2,3], because of their high volumetric energy density, lightweight design, environmental friendliness, and long cycle life.

The ever-growing demand for consumer electronics, such as power banks, mobile phones, laptops, digital cameras, tablets, etc., required by today's information-rich, mobile society [4] as well as the electrification of the automotive sector has led to a significant increase in the demand for LIBs [5]. Presently, LIBs have become a key component of portable, telecommunication, medical, computing, automotive, and entertainment equipment [6]. They have also shown outstanding promise for grid-scale energy storage systems. In electric vehicles (EV) and hybrid electric vehicles (HEV), lithium-ion batteries are significantly preferred over other types of batteries due to their enormous performance and long shelf life [7].

Undoubtedly, LIBs are considered a viable option to meet the ever-increasing demands for portable consumer electronic devices and EVs. To meet this requirement, intensive research is being conducted on increasing the volumetric and gravimetric energy density of LIBs [8] as well as developing high-capacity electrode materials for LIBs.

A relatively small theoretical capacity of graphite (372 mAh·g⁻¹ [9,10]) which is now the most widely used anode in LIBs greatly limits its extensive application [11]. Therefore,



Citation: Pushnitsa, K.; Kosenko, A.; Chernyavsky, V.; Pavlovskii, A.A.; Novikov, P.; Popovich, A.A. Copper-Coated Graphite Felt as Current Collector for Li-Ion Batteries. *Coatings* 2022, *12*, 1321. https:// doi.org/10.3390/coatings12091321

Academic Editor: Alicia de Andrés

Received: 29 July 2022 Accepted: 7 September 2022 Published: 10 September 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). to boost the LIB's performance, alternative promising and high theoretical capacity anode materials are required for the replacement of the currently used graphite. It's a key issue to meet the rising demand for energy storage systems in the coming years.

In recent years, extensive researches have focused on using carbon-based fibers (CFs) as negative electrodes due to their good mechanical properties, flexibility, high electrical conductivity, and ability to intercalate lithium ions [12–17]. CFs are considered as long (generally > 1 mm), self-standing tows fibers with carbon as the basic component. Carbon fibers are seen to be a reasonably good material for structural batteries because they have a high electrical conductivity (up to $2 \times 104 \ \Omega \cdot \text{cm}^{-1}$ [18]) in the axial direction of the fiber. For this reason, there is no need to use current collectors or any conductive materials in the negative electrode in a structural battery.

Compared with conventional electrodes, CF-based yarn and fabric electrodes have many remarkable properties that make them an attractive option for electrical energy storage devices. One of the main reasons why researchers are devoting significant attention to CFs is that it provides fast charge (electrons or holes) transport to metal ions and active materials thanks to their continuous conductive network. In addition, their macroporous structure provides good ion diffusion kinetics and excellent electrolyte infiltration. Moreover, CFs can be used as flexible, lightweight, free-standing, and even structural electrodes without using a conductive agent or polymer binder for different new applications.

The specific capacity of traditional CMFs ranges between $200-300 \text{ mAh} \cdot \text{g}^{-1}$ [6]. Despite the higher capacity of natural graphite (it's theoretical/practical capacity: $372/\sim360 \text{ mAh} \cdot \text{g}^{-1}$), CFs surpass it in terms of electrode capacity and electrode flexibility owing to their reasonably good mechanical and electrical properties which allow them to be directly used as anode materials without conductive agents and a binder.

It is worth mentioning that such a multi-functional, carbon fiber-based material as graphite felt (GF) which is produced by graphitization of CF is also extensively used as current collectors for flexible electrodes of electrochemical energy storage devices. It's three-dimensional (3D) porous structure with high specific surface area [19,20] makes it an excellent choice for a wide range of energy and environmental applications. GF has received a lot of attention recently because of its reasonable electrical conductivity and mechanical flexibility as well as excellent corrosion resistance, reasonable cost, and high porosity and electrochemical stability [21,22]. Therefore, carbon materials like graphite felts have been widely tested as electrodes for various applications that include Li-ion batteries [23], vanadium redox flow batteries [24,25], microbial fuel cells [26,27], supercapacitors [28,29], biofuel cells [30,31], electro-Fenton process [32–34], and so forth.

However, the inherent hydrophobicity of pristine graphite felt leads to the low performance of GF-based electrochemical energy storage devices and its poor electrochemical activity in an aqueous solution [35]. In order to overcome the unsatisfactory electrochemical activity of the pristine GF, it's necessary to modify its surface from hydrophobic to hydrophilic properties. At the same time, the GF should be maintained its own native high electrical conductivity in the process of such modification.

Diverse methods for modifying the GF surface at various conditions, such as nitrogenization treatment [36], plasma treatment [37], thermal treatment [38,39], carbon nanomaterials-based modification [40], chemical treatment [41,42], nanostructural metals [43], and metal oxides [44,45] decorating have been successfully developed and used. A further promising solution to modify the GF surface is the coating of graphite felts with metals by electroplating.

Electroplating is an easy way for the surface modification of CF. It avoids mechanical damage to the fibers. Among other surface modification strategies, electroplating is the least expensive technology. Copper is the metal of choice for most metallic coating for carbon fibers owing to it is non-reactive with carbon, it has good thermal and electrical conductivity, and moreover, interfacial phenomena, such as the intermetallics crystallizations, are negligible [46]. Furthermore, the thickness of the metal coating produced during

the plating changes with the processing time and unlike, for example, the coating with physical vapor deposition (PVD), it's easy to control.

Overall, GF-based electrodes have been the subject of several reviews related to environmental and energy topics. However, the majority of these reviews are devoted only to redox flow batteries and wastewater treatment by electrochemical advanced oxidation processes.

In the present work, we present several structural negative electrodes consisting of copper-modified GFs for LIBs with CR2032 coil-type cells. To the best of our knowledge, this is the first comprehensive report for LIBs in which we compare and discuss the electrochemical characteristics of various GF-based anode materials, such as the pristine GF, graphite-coated GF, copper-coated GF, and GF coated with copper and graphite simultaneously. The composition of the GF-based electrodes and their morphology have been characterized. Electrochemical characterization was carried out to test rate performance, capacity, and the presence of side reactions.

The findings demonstrated that a copper-modified current collector based on graphite felt increases LIB capacity up to $450 \text{ mAh} \cdot \text{g}^{-1}$ and can be used to meet the rising demand for energy storage systems in the coming years. Therefore, we suggest using graphite felt coated with copper as alternative promising and high theoretical capacity anode material for LIBs to replace the currently used graphite anode materials with a relatively small specific capacity.

2. Materials and Methods

2.1. Synthesis of Cu-Coated Graphite Felt Electrode

To create a copper-coated current collector based on graphite felt, commercially available graphite felt was used (supplier ZLWMQMD 001 Store, Guangzhou, China). Commercially available synthetic graphite (artificial graphite powder) (supplier GELON LIB GROUP, Shandong, China) was used as the active material. Arkema's PVDF of the Kynar brand and black carbon Carbon Black brand of the Super P company were used as a binder and conductive additive, respectively, during smearing. N-methyl-2-pyrrolidone (NMP) was used as a solvent for the preparation of a suspension. These materials were not subjected to additional cleaning and processing. Powdered materials were pre-dried under vacuum at a temperature of 70 $^{\circ}$ C for 12 h.

Copper was applied on the felt by electrochemical deposition from an electrolyte of the following composition: 100 g/L of $CuSO_4 \cdot 5H_2O$, 40 g/L of H_2SO_4 with the addition of a surfactant. A 99.99% pure copper plate was used as a counter electrode. Before coating, the carbon fiber was impregnated in the electrolyte by vacuuming the sample in an electrolyte solution. Deposition was carried out at a current density of 0.01 A/cm² geometric surface. Using time variation, 6 samples were obtained with 98.9%, 109.5%, 56%, 54.2%, 19.5% and 15.6% of copper, relative to the original felt mass. The samples were labeled CuGF100, CuGF56, CuGF19.5, CuGF109.5, CuGF50, CuGF20.

The active graphite material was applied to the samples CuGF109.5, CuGF56 and CuGF19.5 by wetting one of the sample surfaces in a suspension of the active material, binder, and conductive additive in a ratio of 92:5:3 respectively. The prepared suspension was leveled up by the spreading machine Dr. Blade to a thickness of 250 microns, after which the sample by one of the sides was immersed in the applied suspension. After this step, the samples were dried at 70 °C for 12 h. The obtained samples were labeled as CuGF100 + C, CuGF50 + C and CuGF20 + C.

2.2. Preparation of Comparative Samples

As comparative samples, the copper foils with applied active material (label C1 and C2), graphite felt samples (labels GF1 and GF2) and graphite felt samples with applied active material (labels GF + C1 and GF + C2) were also prepared.

C1 and C2 samples were prepared by applying active material on the copper foil with thickness of 20 microns. Active material, binder, and conductive additive (black carbon) were mixed to a suspension in a ratio of 92:5:3 respectively. The applying method is

described in Section 2.1 The suspension layer's thickness was 250 microns. After spreading the samples were dried at 70 $^{\circ}$ C for 12 h. Before cutting down the electrodes, the spread was compacted on the rollers, after which the electrodes with a diameter of 15 mm were cut down.

GF1 and GF2 samples were electrodes cut down from graphite felt with a diameter of 15 mm. There were no additional processes for these samples.

The GF + C1 and GF + C2 samples were cut from graphite felt with a diameter of 15 mm with an active material applied to one side. The method of active material applying to the fiber is described in the Section 2.1. After drying, the electrodes were assembled according to the method described above.

The scheme of the main types of investigated samples is presented in Figure 1.



Figure 1. The schematic diagram of all investigated samples.

All samples and the mass distribution of various materials in them are presented in Table 1.

Table 1. Masses of samples and the mass distribution of materials. All masses are in milligrams.

Sample	C1	C2	GF1	GF2	GF + C1	GF + C2	CuGF 20 + C	CuGF 50 + C	CuGF 100 + C	CuGF 20	CuGF 50	CuGF 100
Electrode, mass	41.16	41.39	23.92	22.59	36.42	38.99	47.59	58.70	65.85	26.59	36.15	45.17
Graphite felt, mass	-	-	23.92	22.59	23.68	23.68	24.46	25.76	21.38	23.00	23.45	22.71
Deposited copper. mass	-	-	-	-	-	-	4.78	14.42	23.42	3.59	12.7	22.46
Foil, mass	22.80	22.80	-	-	-	-	-	-	-	-	-	-
Active material, mass	16.86	17.10	-	-	11.68	14.08	16.88	17.04	19.37	-	-	-
Binder, mass	0.90	0.93	-	-	0.68	0.77	0.92	0.93	1.05	-	-	-
Conductive additive, mass	0.60	0.56	-	-	0.38	0.46	0.55	0.55	0.63	-	-	-

2.3. Characterization

The morphology, microstructure, and chemical composition of the samples were studied using Mira 3 Tescan scanning electron microscope with an EDX Oxford Instruments X-max 80 energy dispersive detector for X-ray spectroscopy. X-ray phase analysis was carried out on a Bruker Advance D8 diffractometer in the range of angles from 20° to 100° with a step of 0.02° and an exposure of 1 second at each step. The wavelength was 1.5418 Å. Identification was carried out using DIFFRAC.EVA V5.0 software. Structural parameters were refined using the Rietveld method using TOPAS 4 software.

2.4. Electrochemical Characterization of Samples

To measure the electrochemical characteristics of the samples, CR2032 disk layouts were assembled with a test electrode against lithium metal used as counter electrode. While assembling the layouts, the electrolyte TC-e918 from Tinci company and separator 2325 from Celgard company were used. The layouts were assembled in a glove box with an Argon atmosphere, water, and oxygen content was less than 10 ppm.

To determine the specific capacity of the electrodes, all samples were cycled according to the same method, which is presented in Table 2. For uniform formation of solid electrolyte interphase (SEI) after assembly of the layouts at step 2, all samples were charged with a low current for 10 h. The full discharge of the layout sconsisted of three stages: a discharge current of 10 mA/g to 0.01 V, a discharge current of 5 mA/g to a voltage of 0.01 V, a discharge by an incident current. The samples were charged with a current of 10 mA/g to a voltage of 1.5 V.

No.	Step	Time, min	Voltage, V	Current Density, mA/g *	Process
1	Rest	5	-	-	-
2	Discharge	600	0.01	1	Lithiation, SEI formation
3	Rest	5	-	-	-
4	Discharge		0.01	10	
5	Discharge		0.01	5	Lithiation
6	Discharge		0.01	1	
7	Rest	5	-	-	-
8	Charge		1.5	10	Delithiation

Table 2. Charge-discharge cycling program.

* Current densities were calculated relative to the mass of the electrodes.

Electrochemical measurements of the charge and discharge capacity of the samples were carried out using the Neware coin cell-5 V 10 mA Battery Test System. The cyclovoltamperograms were obtained using a scanning rate of 0.1 mV s⁻¹ at potentials 0–3.0 V. Impedance spectra were taken on a potentiostat in the frequency range from 0.01 Hz to 100 kHz.

3. Results and Discussion

3.1. SEM, EDX and XRD Analysis of Initial Materials and Investigated Samples

Figure 2 shows SEM images of the initial materials and obtained samples.

Initial graphite felt shown in Figure 2a, it exhibits a typical filament structure with chaotically intertwined strands of carbon fiber with a diameter of about 8 microns. Figure 2b shows a sample of CuGF20. Deposited copper particles on the fiber is represented as uniformly distributed crystals of a coarse pyramidal structure. The size of the deposited crystals is less than 10 microns. For the sample CuGF50 (Figure 2c), copper deposition is less uniform. Copper-coated fibers are observed to a greater extent than others. The deposited copper crystals have a size comparable to the crystals on the sample CuGF20. On the sample CuGF100 (Figure 2d), fibers completely coated with copper are observed. The size of the deposited crystals does not exceed the size of the crystals on the two previous samples with deposited copper, however, a large number of smaller crystals are observed, which indicates the predominance of the nucleation process over the crystal growth process under this copper deposition regime. On Figure 2e,f CuGF50 +C sample is presented in the detection mode of secondary (e) and back-scattered (f) electrons. The microstructure of the felt is columnar fibers. The light powder particles observed in the BSE mode are due to the presence of deposited copper. On Figure 2e also nanoscale particles are observed similar in density to the felt material, thus these nanoparticles are presumably graphite.



Figure 2. SEM images of the initial materials and obtained samples: (**a**)–graphite felt, (**b**) CuGF20, (**c**) CuGF50, (**d**) CuGF100, (**e**) CuGF50 + C in SE mode, (**f**) CuGF50 + C in BSE mode.

Figure 3 presents the results of EDX mapping of samples CuGF20 (a), CuGF50 (b) and CuGF100 (c), from which we can understand the relationship of how exactly copper spreads over the felt surface during electrochemical deposition with an increase in the mass of deposited copper. At 20%, copper is deposited point-by-point on the felt, at 50% linearly and at 100% it completely enveloped the fibers of the felt.

Figure 4 shows the phase analysis of the samples. A halo in the region of 25 degrees indicates an amorphous structure of carbon felt. The presence of copper in CuGF50 and CuGF50 + C samples was observed. The presence of powder graphite is also observed in the sample CuGF50 + C. Thus, the difference between carbon felt with a structure of amorphous carbon, and powdered graphite with an obvious structure of graphite is clearly visible.

3.2. Electrochemical Analysis of Samples

The specific capacity is calculated based on the total mass of the negative electrode, unless otherwise specified. Galvanostatic charge curves of the 1st cycle of all investigated samples in the potential range of 0.01 to 1.5 V at different current densities are shown in Figure 5.

Specific capacities of all samples at 1.5 V are presented in Table 3.

Sample	С	GF	GF + C	CuGF20 + C	CuGF50 + C	CuGF100 + C	CuGF20	CuGF50	CuGF100
Specific capacity, mAh∙g ⁻¹	143.5	333	300.8	473	292.6	184.8	254.4	200.4	265.1

Table 3. Specific capacities of all samples at 1.5 V.



Figure 3. EDX -mapping images of copper-deposited graphite felt samples: (a) CuGF20, (b) CuGF50, and (c) CuGF100.



Figure 4. Diffractograms of GF, CuGF50 and CuGF50 + C samples.

If we consider the shape of the charging curves of a graphite anode and a carbon felt sample, we can observe that graphite has the main set of capacity up to 0.25 V with a slight increase in voltage, and then there is an almost vertical line of voltage growth with a slight

increase in capacity. In carbon fiber, the growth goes more smoothly, and it goes to the vertical section only in the region of 1.2 V. At the same time, the specific capacity of this material is greater than that of graphite.



Figure 5. Charge curves of investigated samples.

When carbon fiber is coated with copper, the capacity decreases. At the same time, the shape of the curve remains the same. With an increase in the mass of copper from 20% to 50%, a decrease in capacity is observed. However, for a sample with 100% of the mass of copper, the capacity is comparable to a sample of 20% of the mass.

The capacity of graphite deposited on carbon felt samples (GF + C) is slightly less than that of pure felt, but the nature of the capacity set is completely different. These samples up to 0.25 V show a plateau similar to that observed in graphite (graphite-like plateau), followed by a voltage growth area, but smoother compared to graphite.

In CuGF + C samples the shape of the charge curve differs depending on the mass of the copper coating. The sample CuGF100 + C has a plateau almost identical to that of graphite, but the voltage growth area is somewhat smoother, due to which the final capacity is higher than that of graphite. With a mass of 50% copper, the curve corresponds in shape to the GF + C sample but has a slightly smaller capacity.

With a further decrease down to the the mass of copper up to 20%, the smoothing of graphite-like plateau can be observed. After 0.25 V, the curve is identical in shape to the carbon felt. The specific capacity of this sample is the largest among all the studied electrodes.

Figure 6a shows the cyclic voltamperogramms of the anode made of graphite and carbon felt. It can be noted that the smoother nature of the capacity set, which was noted above, can be noticed here. This may be due to the presence of micro-crystallite composed of several ordered graphene layers [46]. The peak around 0.82 V corresponds to the insertion or extraction of Li in the disordered accommodation vacancy [47,48].

On Figure 6b it can be noted that the position of the peaks for a sample with 50% of the copper mass differs from 20% and 100%: 0.235 V (vs. 0.27 and 0.29 V, respectively) and 0.78 V (vs. 0.8 V). This correlates with what we have observed in the behavior of charging curves.

For CuGF + C (Figure 6c) samples, the position of the most intense peaks is approximately the same for all copper masses, but the shape width decreases with increasing of copper mass. The decrease in width can be interpreted to approximate the behavior to graphite. Note that in these samples, the intensity and position of the second peak on the lower part of the half-curve also change. With an increase in the mass of copper, the



intensity of these peaks decreases, and they shift to the left. This can be attributed to the approximation of the charging curve in shape to graphite.

Figure 6. CVA of the studied electrodes (**a**)-graphite and carbon felt; (**b**)-carbon felt with copper; (**c**)-carbon felt with copper and graphite.

The obtained electrochemical impedance spectra is presented on Figure 7.

It was modeled using an equivalent circuit shown in Figure 8. The RS resistor is responsible for the internal resistance of the measuring cell. The first block consisting of a constant phase element and a resistor connected to it can be associated with SEI parameters. The second block corresponds to the charge transfer processes during intercalation of lithium ions. Table 4 shows the resistances of equivalent circuits for different samples.

Table 4. The resistance of equivalent circuits for different samples.

Sample	С	GF	GF + C	CuGF20 + C	CuGF50 + C	CuGF100 + C	CuGF20	CuGF50	CuGF100
R _S , Ω	4.2	2.8	1.1	1	2.7	5.7	4.3	3.9	4.2
R_{SEI}, Ω	61.2	21.7	57.6	2.8	214.4	21.8	7.2	2.8	5
R_{CT}, Ω	44.6	30	13.9	16.9	119.5	9.7	9.4	6.3	7



Figure 7. EIS of investigated electrodes.



Figure 8. The equivalent circuit for EIS fitting.

It can be mentioned that samples without graphite have less SEI resistance than samples with graphite. This is probably due to a different morphology of the surface. The addition of a copper coating reduces the charge transfer resistance. This can be explained by the higher electronic conductivity of copper compared to carbon. However, it can be noticed that the CuGF50 + C sample is out of the general trends. The RSEI and RCT resistances for this sample are several times greater than for others.

It can be concluded that the copper coating increases the capacity of the samples. Presumably, this effect can be explained by the better electrical conductivity of copper. However, with an increase in the mass of the coating, its continuity also increases, which leads to the isolation of the deposited graphite particles from the surface of the carbon block and changes the nature of the capacity set. So at 50% there is a transition period when the coating already occupies a fairly large area, but not yet solid. At this stage, we see a serious deterioration in performance. However, with a sufficiently solid coating, this electrode behaves like graphite on a copper foil. However, due to the more developed surface, the capacitive characteristics of such electrodes are higher.

4. Conclusions

GF-based anode materials, such as the pristine GF, graphite coated GF, copper-coated GF, and GF coated with copper and graphite simultaneously were successfully obtained and compared. The composition of the electrodes and their morphology have been characterized using X-ray diffraction, scanning electron microscopy and energy-dispersive X-ray spectroscopy methods of analysis. To characterize electrochemical performance such techniques as EIS, CVA and charge/discharge was used.

Samples with a specific capacity of up to $473 \text{ mAh} \cdot \text{g}^{-1}$ were obtained, which exceeds the specific capacity of a conventional graphite anode. It was also found that graphite felt has a different type of capacity set compared to graphite, which is presumably due to differences in microstructure. When graphite and graphite felt are used together, they work synergistically, increasing the capacity. It was also noted that the addition of a copper coating increases the specific capacitance and reduces the resistance to charge transfer, which may be due to the better electronic conductivity of copper. However, with an increase in the mass of the coating, the morphology of the surface and the mechanisms of capacity recruitment change. It was determined that a coating with a mass of about 20% of the mass of the anode is optimal. The obtained materials can be used in LIBS as anodes with a high specific capacity.

Author Contributions: Conceptualization P.N. and K.P.; methodology, A.A.P. (Alexander A. Pavlovskii), K.P. and A.K.; software, K.P. and A.K.; validation, K.P. and A.K.; formal analysis, K.P., A.K. and V.C.; investigation, A.A.P. (Alexander A. Pavlovskii), K.P. and A.K.; resources A.A.P. (Anatoliy A. Popovich) and P.N.; data curation, K.P. and A.K.; writing—original draft preparation, A.A.P. (Alexander A. Pavlovskii); writing—review and editing, K.P., A.K. and V.C.; visualization, A.A.P. (Alexander A. Pavlovskii); supervision, K.P., P.N. and A.A.P. (Anatoliy A. Popovich); project administration, P.N.; funding acquisition, P.N. All authors have read and agreed to the published version of the manuscript.

Funding: The research is funded by the Ministry of Science and Higher Education of the Russian Federation under the strategic academic leadership program "Priority 2030" (Agreement 075-15-2021-1333 dated 30 September 2021).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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