

# Enhancing Lithium-Air Battery Performance through CoPc@CNT Composites: Electrochemical Analysis and Insights

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## Abstract

Cobalt-phthalocyanine (CoPc) catalysts have shown great promise for enhancing the performance of lithium-oxygen (Li-O<sub>2</sub>) batteries, offering benefits such as efficient lithium storage, high reversible capacity, improved cycle performance, and enhanced charge and discharge capacity. In this study, we focused on the synthesis of CoPc-carbon nanotube (CNT) composites with porous structure. The composites were prepared by synthesizing CoPc compounds and interacting them with CNTs using a 3D ball mill shaker. Comprehensive spectroscopic techniques including NMR, FTIR, and UV were employed to characterize the newly synthesized phthalonitrile and phthalocyanine compounds. The surface morphologies of the composite materials were investigated using SEM, EDX, mapping and TEM analysis, enabling the determination of particle sizes and chemical compositions. XRD and XPS analyses confirmed that the composite structures were consistent with the existing literature. BET analysis revealed multilayer isotherm for the composites, indicating their favorable properties. The composite catalysts were incorporated into batteries and their performance was evaluated through various electrochemical tests. Notably, the CoPc1-CNT composite exhibited a remarkable discharge capacity of 3400 mAh g<sup>-1</sup>catalyst in the prepared battery.

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**Keywords:** Li-O<sub>2</sub> batteries, Porous Structure, Composite catalysts, Cobalt Phthalocyanine, Carbon nanotube

### Introduction

Intermittent renewable energy generation poses significant challenges to our energy systems<sup>[1]</sup>. Unlike traditional fossil fuel-based power generation, renewable energy sources such as solar and wind are subject to natural variations and are not constantly available<sup>[2]</sup>. This intermittency creates a mismatch between energy supply and demand, as renewable energy production does not always align with peak energy consumption periods<sup>[3]</sup>. As a result, excess renewable energy may be generated during low-demand periods, while insufficient energy is available during high-demand periods<sup>[4]</sup>. This situation leads to inefficient energy utilization and potential grid instabilities<sup>[5]</sup>. To address these challenges, efficient energy storage solutions are needed<sup>[6]</sup>. Energy storage systems can capture surplus energy during times of high production and release it during periods of high demand, ensuring a more balanced and reliable energy supply<sup>[7]</sup>. By effectively storing renewable energy, we can overcome the limitations of intermittency, enhance grid stability, and promote the wider integration of renewable energy sources into our energy systems. The storage of energy obtained from renewable sources is a matter of great significance in our quest for sustainable power solutions. Fuel cells and batteries, as the forefront of energy storage systems, rely on fundamental components such as electrodes, membranes, and electrolytes or fuels<sup>[8-19]</sup>. Among these technologies, Li-O<sub>2</sub> batteries have garnered immense attention due to their high specific energy reaching approximately 11,425 Wh kg<sup>-1</sup>, making them highly appealing for next-generation energy storage applications<sup>[12-18, 20]</sup>. However, despite their potential, several challenges need to be addressed. Currently, electric vehicles powered by state-of-the-art Li-ion batteries struggle to meet the demand, with limited ranges of less than 100 miles per charge. In contrast, Li-O<sub>2</sub> batteries possess the potential to achieve capacities that can rival those of gasoline vehicles. To fully harness this potential, it is crucial to develop cost-effective and advanced bifunctional electrocatalysts for oxygen reduction reaction (ORR) and oxygen oxidation reaction (OER) in Li-O<sub>2</sub> batteries<sup>[12-18, 20]</sup>. Nonetheless, there are obstacles to overcome. Aprotic Li-O<sub>2</sub> batteries typically consist of a Li metal anode, a porous air cathode, a separator, and an electrolyte that facilitates the migration of Li<sup>+</sup> ions between the electrodes<sup>[21]</sup>. The aprotic electrolytes are liquid solutions of lithium salts dissolved in organic solvents. Within a lithium-air battery cell, a lithium-ion conductive membrane is sandwiched between a lithium metal anode and a porous air cathode. However, Li-O<sub>2</sub> batteries face several technical limitations that hinder their practical implementation. One of the primary challenges is the stagnation of ORR and OER in the aprotic solution. This leads to large discharge overpotentials and overcharge potentials, which reduce the overall energy efficiency of the battery. These overpotentials result from sluggish kinetics and limited catalytic activity, making it difficult to achieve efficient oxygen electrochemistry. Furthermore, electrode and electrolyte instability under high charge potentials poses a significant challenge<sup>[22]</sup>. The high reactivity of lithium metal anodes with the electrolyte can lead to the formation of unstable solid-electrolyte interphase (SEI) layers, hindering ion transport and causing capacity fading over repeated charge-discharge cycles<sup>[22, 23]</sup>. Electrode degradation and dissolution of active materials can also occur, further limiting the battery cycle life and overall performance<sup>[24, 25]</sup>. However, recent studies have shown that the pulsed current can boost the stability of lithium metal anode and improve the performance of lithium-oxygen batteries<sup>[26]</sup>. The choice of suitable electrolytes for Li-O<sub>2</sub> batteries is also crucial. The compatibility between electrolyte and electrode materials as well as the stability of electrolyte at high potentials is vital to prevent side reactions and maintain the battery performance. However, finding electrolytes that exhibit high ionic conductivity, good stability, and low reactivity with electrode materials remains a challenge. Another limitation is the complexity of the oxygen crossover issue<sup>[27]</sup>. Oxygen crossover from cathode to anode can cause parasitic reactions, leading to side reactions and reduced efficiency<sup>[28]</sup>. It can also contribute to the formation of lithium peroxide (Li<sub>2</sub>O<sub>2</sub>) and other unwanted byproducts, which can accumulate and affect the battery performance and capacity<sup>[29, 30]</sup>. In addition to these challenges, the limited understanding of the underlying electrochemical mechanisms and reaction intermediates in Li-O<sub>2</sub> batteries hampers the development of effective strategies for improving their performance and stability. The complex interplay between electrode materials, electrolyte, and catalytic processes requires further investigation and optimization to overcome the limitations of Li-O<sub>2</sub> batteries and enable their widespread practical application.<sup>[11, 31-48]</sup> Additionally, the catalyst support material also holds significance since ORR and OER take place on the catalyst surface. By dispersing the catalyst particles on a support, the surface area is maximized, enabling a more efficient utilization of the catalysts<sup>[8, 18, 45]</sup>. Transition metals, owing to their activity and good conductivity, are

widely employed as catalysts, particularly in the form of nanomaterials for rechargeable Li-O<sub>2</sub> batteries. Carbon, with its high degree of dispersion, good conductivity, and affordability, has emerged as a promising catalyst support material [49-51]. Carbon nanomaterials including nanotubes have garnered considerable attention due to their enhanced capacity and stability, offering distinct advantages over conventional carbon black, such as improved stability and higher conductivity [52]. Moreover, Co-phthalocyanines have shown promising attributes for Li-O<sub>2</sub> batteries, including good coulombic activity<sup>[20, 53]</sup>, favorable lithium storage, high reversible capacity, improved cycling performance<sup>[54]</sup>, increased discharge energy, elevated open circuit potential [55], slow increase in internal pressure, and enhanced charge and discharge capacity<sup>[56]</sup>. Significant advancements have been made in addressing the limitations of Li-O<sub>2</sub> batteries and improving their performance. Previous studies have focused on developing efficient catalysts for oxygen reduction and oxidation reactions, exploring new electrode materials, and optimizing the electrolyte composition. These efforts have led to the discovery of promising catalyst materials such as transition metal compounds and carbon nanomaterials that exhibit enhanced catalytic activity and stability. Moreover, researchers have investigated the use of new electrolytes with improved compatibility and stability. However, despite these advancements, several limitations persist. Challenges such as electrode/electrolyte instability, limited cycle life, and low energy efficiency still need to be overcome. The complex interplay between different components of Li-O<sub>2</sub> batteries necessitates further research to gain comprehensive understanding of the underlying mechanisms and to develop novel strategies for achieving higher performance and reliability. This study aims to investigate the potential of cobalt-phthalocyanine (CoPc) catalysts for Li-O<sub>2</sub> batteries and enhance their performance. The study focuses on using CoPc-CNT (carbon nanotubes) composites with porous structure as catalyst materials. The compounds were synthesized and interacted with CNT in 3D ball mill shaker to form the composites. The synthesized compounds were characterized using spectroscopic methods and the surface morphologies of the composited compounds were examined through SEM, EDX, Mapping and TEM analyses. XRD, BET and XPS analyses were conducted to assess the structures of the composites and verify their compatibility with previous researches. Batteries were prepared using the composite catalysts and their efficiency was evaluated through various electrochemical tests.

## Parts of Experimental

### Preferred Materials and methods

All solvents and reagents which are hexanol (anhydrous, [?]99%), chloroform (CHCl<sub>3</sub>), DMF (N,N-Dimethylformamide, anhydrous, 99.8%), isopropyl alcohol (HPLC grade, 99.9%), acetonitrile (HPLC grade, [?]99.9%), tetrahydrofuran (THF), 4-((trifluoromethyl)thio) phenol, 4-(Imidazol-1-yl)phenol, 4-nitrophthalonitrile, anhydrous K<sub>2</sub>CO<sub>3</sub> ([?]99.0 purity), % 5 NaHCO<sub>3</sub> (Reagent Plus®), [?]99.5%, powder), 1,8-diazabicyclo [5.4.0 ] undec-7-ene (DBU), CoCl<sub>2</sub>, NiCl<sub>2</sub> were purchased from commercial suppliers and used without. FT-IR spectra were recorded using the Perkin Elmer Spectrum 65 model FT-IR Spectrometer. Chromatography was performed using Merck grade 60 silica gel. The purity of the products was assessed at each step by TLC (MeOH/H<sub>2</sub>O (1:1), SiO<sub>2</sub>) and ethyl acetate/hexane (17:3) systems. TLC spots were visualized under a CAMAG model UV lamp. Melting point determinations were conducted using a Gallenkamp model device. UV-vis absorption spectra were obtained using Evolution 220 UV-visible Spectrophotometer with solutions of 1x10<sup>-5</sup>M concentration. Mass spectra were acquired using Agilent 6545 QTOF MS model instrument. NMR spectra were recorded using AVANCE III 400 MHz NaNoBay FT-NMR model device. X-ray measurements were carried out using D8-QUEST diffractometer. SEM, EDX and mapping spectra were acquired using FEI Quanta 650 Field Emission SEM model device. XRD spectra were obtained using Bruker D8 DISCOVER. TEM analyses were conducted using FEI TALOS F200S TEM 200 kV model device. All experiments were performed under a dry N<sub>2</sub> atmosphere. Long-term charge-discharge cycles of the batteries were performed using an 8-channel battery analyzer. The Li-O<sub>2</sub> cell battery tests were conducted using a Gamry interface 1000 potentiostat/galvanostat device within a potential range of 2.5 – 4.5 V under O<sub>2</sub> flow at 1 atm. The interface impedances of the air cathodes were measured before and after the charge and discharge cycles by applying an amplitude of 10 mV in the frequency range of 10<sup>5</sup> – 10<sup>-1</sup> Hz.

### The procedure for synthesis

#### 4-(4-((trifluoromethyl)thio)phenoxy)phthalonitrile(P1) and 4-(4-(1H-imidazol-1-yl)phenoxy)phthalonitrile (P2)

4-(thifluoromethyl)thio)phenol( 5.5 mmol, 1.068g) or 4-(Imidazol-1-yl)phenol (5.5 mmol, 0.881g) and excess of  $K_2CO_3$  (5.78 mmol, 1.903g) were added to dry DMF (11mL) under nitrogen atmosphere and dissolved by mixing. Then, 4-nitrothalonitrile (5.59 mmol, 0.952 g) was added dropwise to the rapidly stirring mixture at 50-60degC (Scheme 1). The reaction mixture was allowed to react for 3 days under nitrogen atmosphere. Afterwards, the reaction mixture was cooled in ice-water mixture (200 cm<sup>3</sup>). The resulting creamy product was filtered and washed with distilled water until neutralization To remove any unreacted products, the solid was dissolved in chloroform and washed with 5%  $NaHCO_3$  solution. The resulting creamy solutions were then dried using anhydrous  $Na_2SO_4$  and the solvents were subsequently removed under vacuum<sup>[57]</sup>. The purity of the reactions was assessed using TLC in a mixture of  $CHCl_3$ :MeOH (100:3). Following purification, the compounds were crystallized in chloroform. Subsequently, the compounds were stored in a vacuum oven at 30degC for one week. **SCHEME 1** Yield (P1): 59.06%. Ma (P1): 320.29 g/mol. Melting Point (P1): 81.2-82.9degC. FT-IR (cm<sup>-1</sup>); 3066 (w, Ar-CH), 2926 (w, Alip-CH), 2229 (C[?]N, st), 1675(C=C), 1578 (C=N), 1487(st), 1253 (Ar-S-Alip CH), 1078, 1013, 950, 850, 824. <sup>1</sup>H NMR( $CDCl_3$ , ppm): 7.79-7.76 (d, 2H, phenyl) 7.74(s, 1H, phenyl), 7.36 (d, 2H, phenyl), 7.32 (d, 2H, phenyl) 7.14 (d, 2H, phenyl). EI/MS m/z: 321.026 [M]<sup>+</sup>. Yield (P2): %70.47. Ma(P2): 286.29g/mol. Melting Point (P2): 130.2-133.1degC. FT-IR (cm<sup>-1</sup>); 3026 (w, Ar-CH), 2920 (w, Alip-CH), 2259 (C[?]N, st), 1675(C=C), 1590 (C=N), 1481(st), 1081, 1013, 947, 841, 810. <sup>1</sup>H NMR( $CDCl_3$ , ppm): 7.87(s, CH, phenyl), 7.78(d, CH, phenyl), 7.52(d,2CH, phenyl), 7.34(d, CH, phenyl), 7.32(d, CH, phenyl), 7.27(d, CH, phenyl), 7.24(s, CH, phenyl), 7.22(d, 2CH, d). EI/MS m/z: 287.099 [M]<sup>+</sup>.

#### Synthesis of (2(3), 9(10), 16(17), 23(24) – tetrakis(4-(4-(trifluoromethyl)thio)phenoxy)phthalocyaninato- metal free) (Pc1) and its Co Compound(CoPc1)

4-(4-((trifluoromethyl)thio)phenoxy)phthalonitrile (1.128 mmol, 0.361g) without salt or anhydrous  $CoCl_2$  (0.282 mmol, 0.0366g) was added to dry hexanol (4 mL) and dissolved by stirring under nitrogen at 160degC, then degassed DBU (1.128 mmol, 0.168 mL) was added dropwise (Scheme 2). The reactions continued at 160 degC for 5 days under nitrogen. The greenish dark blue products were cooled to room temperature after diluting with hexane. The products were repeatedly washed with MeOH and i-PrOH followed by  $CH_3CN$  <sup>[57]</sup>. The purity of Pc1 and CoPc1 was checked by TLC (Hexane: Ethylacetate) (17/3). The presence of double spots indicated that P1 remained partially unreacted in the medium. After Pc1 and CoPc1 were dissolved in approximately 1 mL of chloroform, they were loaded onto the chromatograph and separated by a fractionated column. Firstly, they were run with hexane/ethyl acetate (10:1) and the leading impurity phases were removed, and the remaining parts were taken from the chromatotrome with 5:1 hexane/ethyl acetate. To avoid the loss of yields, the remaining parts of Pc1 and CoPc1 were removed with chloroform in the chromatotrome, which was cleaned with methanol. **SCHEME 2** Yield(Pc1): 9.3%. Ma(Pc1): 1347.34 g/mol, Melting point (Pc1): 205.1-207.8degC. FT-IR (cm<sup>-1</sup>); 3059 (w,Ar-CH), 2925 (Alip-CH), 1580 (C=N), 1568 and 1213 (Ar-S-Alip-CH), 1066, 993, 822, 724. EI/MS m/z: 1348 [M]<sup>+</sup>. Yield(CoPc1): %7.2. Ma(CoPc1):1404.1581 g/mol, Melting point (CoPc1): 265.1-267.8degC. FT-IR (cm<sup>-1</sup>); 3010 (w,Ar-CH), 2905 (Alip-CH), 1620 (C=N), 1500 and 1120 (Ar-S-Alip-CH), 966, 943, 822, 724. EI/MS m/z: 1404 [M]<sup>+</sup>.

#### Synthesis of (2(3), 9(10), 16(17), 23(24) – tetrakis 4-(4-(1H-imidazol-1-yl)phenoxy)phthalocyaninato- metal free) (Pc2) and its Co Compound(CoPc2)

4-(4-(1H-imidazol-1-yl)fenoksi)ftalonitril (1.128 mmol, 0.322 g) without salt or anhydrous  $CoCl_2$  (0.282 mmol, 0.0366g) was added to dry hexanol (4 mL) and dissolved by stirring under nitrogen at 160degC, then degassed DBU (1.128 mmol, 0.168 mL) was added dropwise (Scheme 3). The reactions continued at 160 degC for 5 days under nitrogen. The greenish dark blue products were cooled to room temperature after diluting with hexane. The products were repeatedly washed with MeOH and i-PrOH followed by  $CH_3CN$ <sup>[57]</sup>. With the mixture of (MeOH:H<sub>2</sub>O)(1:1), Pc2 and CoPc2 were purified from impurities and single spots were obtained. **SCHEME 3** Yield(Pc2):12.6%. Ma(Pc2): 1211.34g/mol. Melting point (Pc2):>280degC. FT-IR

( $\text{cm}^{-1}$ ); 3059 (w,Ar-CH), 2925 (Alifatik-CH), 1580 (C=N), 1568, 1066, 993, 822 and 724. EI/MS  $m/z$ : 1211[M]<sup>+</sup>. Yield(CoPc2): 7.8%. Ma(CoPc2): 1268.4075 g/mol. Melting point(CoPc2): >280degC FT-IR ( $\text{cm}^{-1}$ ); 2950 (w,Ar-CH), 2870 (Alip-CH), 1680 (C=N), 1510, 1120, 963, 850 and 724. EI/MS  $m/z$ :1269 [M]<sup>+</sup>.

### Synthesis of CNT-MPc (Carbon Nanotube supported Metalphthalocyanine) Composites

A homogeneous and nanosized composite was obtained by mixing metalphthalocyanine (CoPc1 or CoPc2) and CNT in equal weight<sup>[58]</sup> for 2 h with 3D mechanical mixer at 1200 rpm.

### Preparation of cathode material for Battery Tests

The MPc-CNT composite and PVDF were mixed in the ratio of 95:5, respectively using 3D ball milling for 6 hours. Subsequently, a slurry was prepared by adding NMP (N-Methyl-2-Pyrrolidinone). The prepared slurry was then subjected to ultrasonic treatment in an ultrasonic bath at 55 degC for 30 min. The cathode material was obtained by applying the slurry onto a nickel foam (radius 16 mm) using the roll coating technique. Before coating, the Ni foams underwent preprocessing step by immersing them in 3.0 M HCl in an ultrasonic bath for 30 min. The Ni foams were then washed with distilled water and further treated with acetone in an ultrasonic bath for 30 min. After drying at 110degC and storing in a desiccator, the Ni foams served as the current collector. The dried Ni foams were loaded with 31.57 mg slurry for CoPc1-CNT and 18.91 mg for CoPc2-CNT, respectively. Following overnight drying at 70degC, the Ni foams were left in the desiccator for 5 min before being transferred to a glove box for battery preparation. Batteries were assembled using 20 mm diameter separator, 16 mm diameter Li anodes, 19 mm diameter cathode and 1.0 M LiPF<sub>6</sub> in DMSO electrolyte.

## Results and discussions

### Evaluation of <sup>1</sup>H-NMR Spectra

The NMR spectra of aryl-substituted phthalonitrile compounds typically exhibit polysubstituted peaks resembling those of monosubstituted benzene, typically appearing at approximately  $\delta=7.90-7.00$  ppm. The NMR spectrum of the P1 molecule, as shown in Figure 1a, reveals peaks corresponding to the protons labeled as 1 (CH, d) and 2 (-CH, s) in the range of 7.79–7.75 ppm. Additionally, in the provided spectrum, the peaks for the protons numbered 3 (CH, d) and 4 (2-CH, d) were observed in the range of 7.36–7.26 ppm, while the peak for the 5 (2-CH, d) proton appeared at 7.14 ppm. The integral areas and observed peaks in the spectrum indicate the successful synthesis of P1.<sup>[57]</sup> Upon analyzing the NMR spectrum of the P2 compound, as depicted in Figure 1b, peaks corresponding to the protons labeled as 1-8 (from 1 to 8) were observed at chemical shifts of 7.8, 7.79, 7.52, 7.34, 7.32, 7.27, 7.244, and 7.21 ppm, respectively <sup>[57]</sup>. The presence of these peaks provides confirmation of successful synthesis of the product. The agreement between observed peaks and integral areas further supports the synthesis of the product.**FIGURE 1.**

### Evaluation of FT-IR Spectra

Phthalonitrile and Phthalocyanine compounds were also characterized by FT-IR spectroscopy and the spectra are given in Fig. 2-3. When the literature is reviewed, it is seen that the vibration of C[?]N is approximately 2200  $\text{cm}^{-1}$ , Ar-C is between 3200 and 2950  $\text{cm}^{-1}$ , and Alip-CH is between 2950 and 2800  $\text{cm}^{-1}$ <sup>[57]</sup>. In this study, the characteristic C[?]N peak for phthalonitrile compounds coded as P1 and P2 was observed at 2229 and 2259  $\text{cm}^{-1}$ , respectively. During the cyclotetramerization of P1-P2 to Pc1-Pc2, the sharp CN peak at 2229 and 2259  $\text{cm}^{-1}$  disappeared, respectively. When the IR spectra of Pc1, Pc2, CoPc and CoPc2 were examined, they were obtained very similar to the spectra of the starting materials (P1 and P2) except for minor vibrational shifts. It was observed that the C= N peaks of Pc1 and Pc2, which were observed around 1580 in the FT-IR spectrum, shifted to 1620  $\text{cm}^{-1}$  in metalphthalocyanines called CoPc1 and CoPc2. The weak N-H peaks observed in phthalonitriles named P1 and P2 were not observed in the phthalocyanine and metalphthalocyanine yields. The flat peak observed around 3500 in Pc2 compound was obtained due to humidity. The fingerprint region in metalphthalocyanine compounds (CoPc1 and CoPc2) was shifted to the right when compared to free phthalocyanines (Pc1 and Pc2). The observed peaks were consistent with the literature, indicating that the compounds were synthesized<sup>[57]</sup>.**FIGURE 2 AND 3**

## UV-measurement

It is known that there are two distinct regions in the UV-vis spectra of phthalocyanine complexes, attributed to  $\pi$ - $\pi^*$  transition from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital) of the Pc ring (Q-band) and deeper  $\pi$ - $\pi^*$  transitions (B-Band; UV region). The Q Band is observed around 650-700 nm while the B Band is observed around 300 nm. Based on this information, only B bands were observed around 300 and 290 nm respectively in the UV spectrum of P1 and P2 compounds (Fig. 4-5). When the UV spectrum of P1 and Pc2 compounds is compared with that of P1 and P2 compounds, it is seen that there are also Q bands in the spectrum at 670 and 680 nm, respectively. When the UV spectra were examined, the Q band for CoPc1 was observed at 640(Qx) and 680(Qy) nm, while the Q band for CoPc2 was observed at 650(Qx) and 690(Qy) nm. In the spectrum, the Q bands of CoPc1 and CoPc2 were observed more intensely than the Q bands of Pc1 and Pc2. These results were found to be in agreement with the literature<sup>[59, 60]</sup>. **FIGURE 4 AND 5**

## Surface Morphology

The successful binding of CoPc1 and CoPc2 on the carbon nanotube was confirmed by scanning electron microscopy (SEM). The SEM micrographs seen in Fig. 6(a-b) show the morphologies of CoPc1 and CoPc2 loaded onto CNT surfaces. The bonding of MPc (CoPc1 and CoPc2) on carbon surfaces via intermolecular interactions can be explained as a possible cause of diverse loading of MPc<sup>[61]</sup>. The bonding between the aromatic structure of the carbon surface and the macrocyclic ligand of MPc is a non-covalent  $\pi$ -p interaction<sup>[58]</sup>. Energy dispersive X-ray (EDX) analysis (Fig. 6c-d) was used to determine the chemical composition of the prepared CNT\_MPc composites. Fig. 6(c) EDX spectrum showed successful fixation of CoPc1 on the carbon composite and the presence of C, N, O, F, S and Co elements. The elemental analysis of the CoPc1-CNT and CoPc2-CNT compounds and the corresponding weight percentages are shown in the table overlaid on Fig. 6c and 8d. Fig. 6(d) EDX spectrum shows the successful fixation of CoPc2 on the carbon composite similar to that of CoPc1 and the presence of the elements C, N, O and Co. The presence of desired elements in accordance with EDX and the homogeneous distribution in the mappings of CoPc1 and CoPc2 seen in Fig. 6(e-f) show that the composite has been synthesized. **FIGURE 6** TEM micrographs of CoPc1-CNT (a) and CoPc2-CNT (b) composites are given in Fig. 7. It is clear from the TEM micrographs that the metalphthalocyanines are loaded onto the CNT. In general, metalphthalocyanines interact strongly with oxygen functional groups and oxygen to create complexes<sup>[58]</sup>. The loading of MPc on the carbon surface also depends on the entity of functional oxygen groups in the CNT. CoPc1-CNT and CoPc2-CNT composites exhibit similar property with relatively smaller metalphthalocyanine particles appearing mostly inside the nanotubes. CoPc1-CNT and CoPc2-CNT composites have relatively smaller metalphthalocyanine particles mostly appearing inside the nanotubes. The TEM micrograph shows the interplanetary spacing and particle size of MPc-CNT molecules for CoPc1 and CoPc2, respectively, in the range of about 26.7–66.9 nm and 17.0–37.5 nm. **FIGURE 7**

## XRD

Fig. 8 shows XRD plots of multiwalled CNT composites of CoPc1 and CoPc2 taken between 10 and 90°. Due to severe plastic deformation caused by high-energy ball impacts, the compounds lost their crystallinity and wider XRD peaks were observed<sup>[62]</sup>. In addition, the semi-amorphous structure of the composites causes the peaks to be flat. According to the information obtained from the literature, CNT exhibits diffraction peaks at  $2\theta = 26^\circ$  and  $43^\circ$  corresponding to the graphite planes of (002) and (100)<sup>[63]</sup>. However, the definitions of the peaks seen are given below with reference card numbers. Looking at the reference PDF cards, it is understood that the structure contains Metal-phthalocyanine and CNT composite.  $13.163^\circ$ ,  $21.622^\circ$ ,  $25.397^\circ$ ,  $26.505^\circ$ ,  $34.459^\circ$ ,  $37.917^\circ$ ,  $40.304^\circ$  and  $44.066^\circ$  (Carbon Nitride) - Reference No: PDF 01-087-1526.  $19.075^\circ$ ,  $25.230^\circ$ ,  $29.317^\circ$ ,  $34.102^\circ$ ,  $36.313^\circ$ ,  $37.871^\circ$ ,  $38.638^\circ$ ,  $38.707^\circ$ ,  $39.702^\circ$ ,  $40.1711^\circ$ ,  $40.617^\circ$ ,  $40.740^\circ$  and  $42.822^\circ$  (Cobalt Oxalate,  $\text{CoC}_2\text{O}_4$ ) - Reference No: PDF 00-037-0719.  $21.984^\circ$  and  $31.704^\circ$  (Tetracyanoethylene,  $\text{C}_6\text{N}_4$ ) - Reference No: PDF 00-037-1895.  $33.794^\circ$  (Nitrogen, N) - Reference No: PDF 01-082-2781.  $25.919^\circ$  and  $42.959^\circ$  (Carbon Nanotube) - Reference No: PDF 00-058-1638. **FIGURE 8**

## XPS analysis

XPS provided an opportunity to further investigate the elements and chemical states on the surface of CoPc1-CNT and CoPc2-CNT composites. The XPS spectrum (Fig. 9) showed C, O and N peaks on the surface of CoPc1-CNT and CoPc2-CNT composites. According to the XPS data in Table 1 for CoPc1-CNT composite, the percentages of C, O, N, F, S2p and Co2p atoms on the surface for CoPc1-CNT composite reflect 80.4%, 6.8%, 4.4%, 5.4%, 1.8% and 0.6%, respectively. According to the XPS data in Table 1 for CoPc2-CNT composite, the percentages of C, O, N and Co2p atoms on the surface for CoPc1-CNT composite reflect 83.3%, 8.2%, 6.6%, and 0.3%, respectively. When the XPS spectrum (Fig.9) obtained for the two composites is examined, the peaks for C1s, O1s and N1s were obtained at approximately 285 eV, 395 eV and 530 eV, respectively, and this agrees with the literature<sup>[64, 65]</sup>. **FIGURE 9**

## Electrochemical Tests

The electrochemical performances of the constructed CoPc1-CNT and CoPc2-CNT composite were first investigated in a three-electrode system in 0.5 M LiClO<sub>4</sub> (15g ethylene carbonate + 15g diethylene carbonate) electrolyte. Fig. 10 displays the CV curves at a scan rate of 0.10 V s<sup>-1</sup>. The Ni Mesh graph shows the conversions of 1, 2 and 3 numbers. 1 is Ni/Ni<sup>2+</sup>, 2 is Ni<sup>2+</sup>/Ni<sup>8/3+</sup>, and 3 is Ni<sup>8/3+</sup>/Ni<sup>3+</sup>. When the CV curves shown in fig. was examined, it was observed that different peaks were observed in CoPc1-CNT and CoPc2-CNT composites because of the closed surface with composite materials unlike the voltammogram of Ni Mesh, and the current increased compared to the bare Ni Mesh electrode in the same potential range. The peaks of the CoPc composites are shown as 1 and 2 for oxidation and 1' and 2' for reduction conversions. The 1, 1' are the Co/Co<sup>2+</sup> conversion and 2, 2' are the Co<sup>2+</sup>/Co<sup>3+</sup> conversions. The increase in the current and the observation of the oxidation peaks proved the accuracy of the work done. **FIGURE 10** According to the EIS graph given in Fig. 11, the Ni mesh base material was given the highest resistance. After coating the Ni mesh with CoPc1-CNT and CoPc2-CNT composite materials, the resistance ratios given as the inset figures. As can be seen from the impedance measurements, the charge transfer resistance is smaller for the CoPc1-CNT composite than CoPc2-CNT. **FIGURE 11** Adsorption isotherms have specific isotherms that can be classified between type I and type VI according to IUPAC. The distinctive tendencies of the adsorption isotherms depend on the nature of the pore structure, the adsorption mechanism and the adsorbent/adsorbate interactions. Each type of adsorption isotherm appears to have unique ability to adsorb water vapors within a certain range of relative humidity (RH) or relative pressure (P/Po). Since the adsorption isotherms of CoPc1-CNT and CoPc2-CNT the composites seen in Fig. 12 illustrate the Type-VI, which sign multilayer isotherm absorption<sup>[66]</sup>. **FIGURE 12** The charge/discharge curves of CoPc1-CNT and CoPc2-CNT the composites shown in Fig. 13, provide valuable insights into their electrochemical performance. For the CoPc1-CNT composite, the charging process exhibited a capacity of approximately 2000 mAh g<sup>-1</sup> within the potential range of 3.2 V to 4.5V. During the discharge phase, the potential ranged from 4.0 V to 2.0 V. Notably, an abrupt drop in capacity was observed initially reaching around 500 mAh g<sup>-1</sup>. Subsequently, a stable discharge region spanning from 500 mAh g<sup>-1</sup> to 3000 mAh g<sup>-1</sup> was observed followed by a final decrease in capacity until reaching 2.0 V. Overall, the CoPc1-CNT composite exhibited discharge capacity of 3400 mAh g<sup>-1</sup>. Capacities were calculated according to catalyst weight. In contrast, the charge/discharge curve of the CoPc2-CNT composite, as depicted in Fig. 13, displayed a lower capacity of approximately 1100 mAh g<sup>-1</sup> during charging within the potential range of 3.1 V to 3.85 V. The discharge phase spanned from 3.1 V to 2.0 V with a discharge capacity of approximately 1400 mAh g<sup>-1</sup>. Notably, an initial increase followed by a sudden decrease in charge curve of CoPc2-CNT composite was observed. This behavior can be attributed to a weak bond between the Co metal and the Pc2 leading to an additional redox reaction and subsequent oxidation of the metal. The observed differences in capacity and behavior between CoPc1-CNT and CoPc2-CNT composites highlight the influence of the phthalocyanine structure on the electrochemical performance of composite materials. The higher capacity and more stable discharge behavior of the CoPc1-CNT composite show a stronger interaction between CoPc1 and CNT, leading to improved charge transfer kinetics and enhanced battery performance. These findings emphasize the importance of rational design and selection of phthalocyanine materials for composite electrode applications as they directly impact the electrochemical performance of Lithium-air batteries. Further investigations are needed to gain a deeper

understanding of the underlying mechanisms and optimize the composite composition to unlock the full potential of phthalocyanine based composites for advanced energy storage systems. **FIGURE 13**

## Conclusion

In this study, CoPc@CNT composites were successfully synthesized by interacting two different phthalocyanines, Pc1 and Pc2, with CNT. The synthesized phthalocyanines were characterized using spectroscopic methods and employed in the fabrication of Lithium-air batteries. Various electrochemical tests were conducted to assess the performance of the prepared batteries. As anticipated, the CoPc1-CNT and CoPc2-CNT composites exhibit characteristic oxidation and reduction peaks corresponding to Co/Co<sup>2+</sup> and Co<sup>2+</sup>/Co<sup>3+</sup> redox processes. Impedance measurements revealed that CoPc1-CNT composite exhibited lower charge transfer resistance compared to CoPc2-CNT. BET analysis indicated that both CoPc1-CNT and CoPc2-CNT composites exhibited multilayer isotherm absorption. Furthermore, the battery using the CoPc1-CNT composite demonstrated a charging capacity of 2000 mAhg<sup>-1</sup> and a discharge capacity of 3400 mAh g<sup>-1</sup> catalyst. On the other hand, the battery incorporating the CoPc2-CNT composite exhibited lower efficiency. These findings provide that the CoPc1-CNT composite holds promise for enhancing the performance of lithium-air batteries. Overall, this study successfully demonstrated the synthesis of CoPc@CNT composites, characterized their electrochemical properties, and evaluated their performance in Lithium-air batteries. Further investigations are warranted to optimize the composite composition and explore its potential for advanced energy storage applications. **Acknowledgment** The Scientific and Technological Research Council of Turkey (TUBITAK) (Project No: 118C472) supported this study. The authors thank TUBITAK, Osmaniye Korkut Ata University, and OKUMERLAB.

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**LIST OF TABLE** Table 1. XPS data for CoPc1-CNT and CoPc2-CNT

| Atomic%   | Atomic% | Atomic% | Atomic% | Atomic% | Atomic% | Atomic% |
|-----------|---------|---------|---------|---------|---------|---------|
|           | C       | O       | N       | F       | S2p     | Co2p    |
| CoPc1-CNT | 80.4    | 6.8     | 4.4     | 5.4     | 1.8     | 0.6     |
| CoPc2-CNT | 83.3    | 8.2     | 6.6     | -       | -       | 0.3     |

















