



Processing of carbon fiber/ PFA composite material as electrode of Fuel cells and batteries

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ABSTRACT

Highly porous Carbon fiber performs have been impregnated with Poly-Furfuryl alcohol (PFA) by insitu catalytic polymerization of FA. The samples are further pyrolyzed at 600 – 2400 °C in an inert atmosphere to form carbon-carbon composite. The samples were further subjected to intensive electrical and mechanical characterization. Higher heat treatments results in graphitization of the matrix phase leading to increased conductivity. This can probably result in samples with good electrode properties for cells and batteries.

Keywords: PFA, Catalyst, Heat Treatment, Electrical Conductivity

Introduction

Electrode material is the most important and costly part of a battery and fuel cell.^{1,2} Development of suitable low density Electrode material is important due to the need to maintain high electrical conductivity, good mechanical strength, and low manufacturing cost.^{2,3} Graphite is a well-known conventional electrode material. Now-a-days a number of other carbon precursors are being employed to overcome the shortcomings of graphite. Porous conducting carbon paper has been employed as electrode for both fuel cell⁴ and li-ion batteries.⁵

To obtain a carbon/carbon-Anode materials, the carbonization (or pyrolysis) of suitable carbon containing materials such as polyfurfuryl alcohol (PFA), phenolic resin, polymer polyimides, phenol formaldehyde, polyacrylonitrile and others, is normally performed under inert atmosphere or vacuum.⁶ Polyfurfuryl based electrode exhibit attractive distinguish properties because of their excellent porosity, good conductivity, good thermal stability, and high corrosion resistance.^{7,8} In the present study PFA has been prepared by insitu catalytic polymerization of FA. The objective of this work was to study the convenience of making carbon based electrode and optimizing it in different temperatures (600-2400 °C) and compositions.^{9,10}

Experimental Section

Materials. A porous carbon fibre preform was prepared with polyacrylonitrile(PAN)-based Toray carbon fibres (T-300). Furfuryl alcohol(obtained from LobaChemie PvtLtd.) was used as a carbonaceous resin for making the composite

paper with 98% purity. Iso-propyl alcohol (obtained from 'Rankem Pvt. Ltd.) was used as a solvent. The preference given to the carbon fibres was based on their high electrical conductivity and high strength so as to enhance the overall conductivity and strength of the composite paper.

Preparation of carbon paper. Carbon fibres were chopped in definite lengths. The chopped carbon fibres were dispersed in an aqueous medium using an emulsifier, which is an acid containing, cross-linked acrylic emulsion copolymer. For that the emulsion is first diluted with distilled water containing chopped carbon fibre and then neutralized with a base. This causes each emulsion particle to swell greatly. The emulsion clarifies under these conditions and become highly viscous. The rate of reaction between the emulsifier and the base is rapid and only a moderate agitation is required for the same. The pH of the final solution was controlled to nearly 7.5 - 8. Addition of excess alkali should be avoided, since pH 10 or higher may cause undesirable change in properties of the emulsifier. The solution is then subjected to stirring using a twin –blade mechanical stirrer for nearly one and half hours.

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Highlights

1. Porous conducting carbon composite electrode material has been developed.
2. Carbon fiber preform structure imparts strength as well as porosity to the final product.
3. PFA has been used as a binder by in-situ polymerization of FA
4. Amount of resin used and HTT plays an important role in determining the properties of composite material.
5. Higher heat treatments leads to graphitization of the carbon fiber/ matrix interface.

Addition of emulsifier and stirring are the two important factors which work together, resulting in the separation of individual filaments from the carbon fibre tow and the uniform dispersion of carbon fibres in water. The slurry, containing well-dispersed chopped carbon fibres was poured into the container of a specially designed filtration unit shown in Fig. 1.

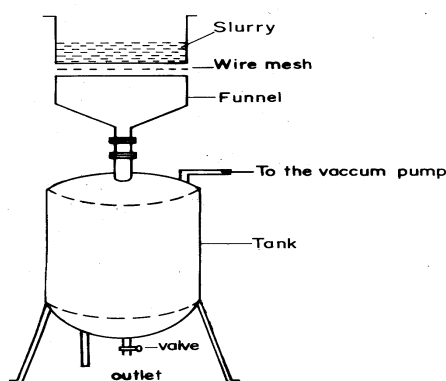


Figure 1. Schematic diagram of filtration unit for making porous carbon fibre preform.

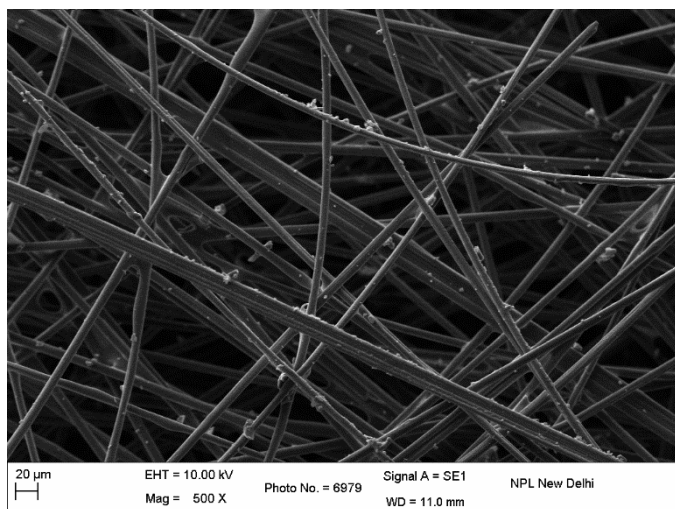


Figure 2. SEM image of a carbon fiber preform.

The water was drained off by creating vacuum in the tank with the help of a rotary pump.

The carbon fibre mat or preform so formed was lifted from the mesh and then dried at room temperature. The density of the porous carbon fibre preform thus prepared is < 0.2 g/cc. The SEM image of the porous carbon fibre preform is shown in fig. 2.

Preparation of PFA based carbon paper. Carbon fibre preforms were impregnated by using polyfurfuryl alcohol and using sulphuric acid/oxalic acid as catalyst. Poly-furfuryl alcohol is not commercially available. It was synthesized in-situ by polymerization of furfural alcohol.^{11,12} The carbon fibre preform was impregnated with calculated amount of Furfuryl alcohol resin using hand lay-up process that allows the paper to be subsequently moulded to a desired thickness and density. The impregnating set up simply consists of a glass plate and a glass rod for uniform impregnation of resin into the carbon fibre preform. Calculation of the volume % of the resin for impregnation was made keeping in view the char yield of the neat resin, which was found to be nearly 45-50 %. The preform was placed on the glass plate and the resin solution was uniformly poured over it, so that the preform is just soaked with the resin solution. Further uniformity was achieved by rolling the glass rod over the soaked preform. The samples were dried at room temperature to remove the solvent (Iso-propyl alcohol). The degree of polymerization is sufficient so that there is very little resin flow during the subsequent moulding step. In the following text whenever the matrix contents in the composite paper is mentioned these refer to the carbonized resin only i.e. volume of the carbonized matrix obtained after heat treatment to 600°C & more than 600°C . This has been referred to as “matrix” in the following text.

The impregnated carbon fibre preform was then moulded into sheet by compression moulding technique. For that the samples were placed in between a specially designed die, made from die steel material. Two dies were used in the experiments performed, one for $10\text{ cm} \times 10\text{ cm}$ sample size and another for $20\text{ cm} \times 20\text{ cm}$ sample size. The die mould was placed in between the platens of the hydraulic press. PLC controlled four pillars; down stroke hydraulic press was used for pressing the carbon paper samples. Compression moulding was carried out at 90°C , i.e. at the gelling temperature of the resin and at a pressure of $50\text{--}70\text{ Kg/cm}^2$. Following moulding, a post-cure is performed at 150°C for 2 hours in air to ensure full curing and cross-linking of the furfuryl resin before carbonization. The methylene bridges between furfuryl molecules cross-links the resin into three-dimensional network leading to formation of rigid structure. The sample so obtained is termed as the composite paper. The sample was characterized for the resin uptake, porosity, density, and fibre/resin volume ratio.

Carbonization/graphitization of the composite. The green samples produced by the above method were carbonized to different temperatures (HTT) viz. 600°C , 1000°C and 2400°C respectively in an inert atmosphere with different heating rates. In one set of experiments the rate of pyrolysis was kept at 10°C/hr till 600°C and thereafter @ 90°C/hr . Faster heating rates not only makes the process cost effective but also helps in the formation of effective porosity in the matrix.

Electrical resistivity analysis

The electrical resistivity (ρ) of the carbonized and graphitized paper was measured using the four-probe

technique. A Keithley 224 programmable current source provided the current. The voltage drop was measured with a Keithley 197 Auto ranging microvolt DMM. The carbon fiber preforms were cut into rectangular strips of size 80mm (length) and 10mm (width). The current was passed along the length of the strip and the voltage drop was measured across different points separated by unit length. The values reported in the text are an average of about 15 readings over the whole surface of the strip.

Measurement of flexural strength of composite paper

The flexural strength of the carbon paper samples was measured on an INSTRON machine model - 4411 according to ASTM: D 1184-69: 'Flexural Strength of Adhesive Bonded Laminated Assemblies'. The span length was kept at 10mm to maintain the span: depth ratio of the test piece at 30:1. The crosshead speed was maintained at 0.5mmmin⁻¹. The properties reported in the text are an average of five readings.

Porosity measurements

The porosity of each carbon paper sample was determined by the kerosene density method. The bulk density (*Bd*) and the kerosene density (*Kd*) of the sample were measured with a Mettler balance, Model ME - 40290 using Archimedes principle. The porosity was calculated by applying the following formula:

$$\text{Porosity} = (1 - Bd/Kd) \times 100\%$$

Raman Spectroscopy

Raman spectroscopy was carried out using a Renishaw in-Via Reflex Micro Raman Spectrometer equipped with the CCD detector at room temperature and in air. Argon ion laser (excitation line 514 nm) was used to excite the samples. One scan per sample was recorded wherein the sample was exposed to the laser power of 25 mW for 30 sec. Raman spectroscopy is a useful tool which has been widely used to characterize the quality and type of tubes. Raman scattering is an inelastic scattering of light whereby the measure of the intensity of the scattered light as a function of its frequency downshift gives the phonon frequency of the material.¹³

Synthesis of electrode with varying amount of Resin.

Carbon fibre preforms were weighted on analytical balance. Solution of furfuryl alcohol in Iso-Propyl alcohol with sulphuric acid as a catalyst is prepared. Samples were prepared with varying amount of resin such that volume ratio of FA/Carbon varied from 4 to 8 times. That is, in this experimental series the volume of furfuryl alcohol was taken 4 times of the volume of carbon fibre for first sample, 5 times for the next sample and so on. Furfuryl alcohol (mixed with required quantity of Iso-propyl alcohol) and catalyst were kept in the sonicator for sonication for 2 to 3 minutes. The impregnating set up simply consists of a glass plate and a glass rod for uniform impregnation of resin into the carbon fibre preform. The preform was placed on the glass plate and the resin solution was uniformly poured over it, so that the preform is just soaked with the resin solution. Further uniformity was achieved by rolling the glass rod over the soaked preform. As already discussed previously the samples were compression moulded and heat treated to 600 °C.

Effect of heat treatment temperature on carbon composite paper. For carbonization, the impregnated and moulded samples are packed between graphite plates. In between every sample a graphite paper/foil is placed so that the papers do not stick to one another. After packing all the samples, the samples were tied by a carbon fiber tow tightly. The packed samples were heated in a muffle furnace up to 600 °C, 1000 °C, 2400°C with a heating rate of 10 °C/hr up to 600°C and thereafter at 90°C per hour. The samples must be heated in the inert condition so argon gas is used for making the furnace environment inert. After reaching at final temperature the furnace temperature was kept on hold for 10 minutes. The samples were then allowed to cool naturally. After carbonization, samples were again weighted.

Property of carbon paper with varying amount of resin.

Electrical Resistivity

Study of electrical resistivity of Carbon paper with increasing amount of Resin: As shown in Fig. 3(a), the electrical resistivity of the composite paper decreases with increasing matrix content. This is quite contrary to previous results reported with other resin systems. This is probably because the electrical resistivity of the carbon fiber is very less (0.0017 ohm cm) as compared to that of PFA. Since the samples are carbonized to only 600 °C complete carbonisation of the resin does not take place, thus resulting in an increased resistivity with resin amount.

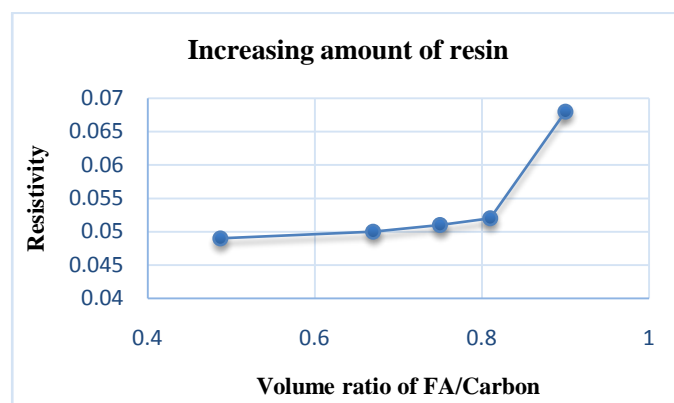
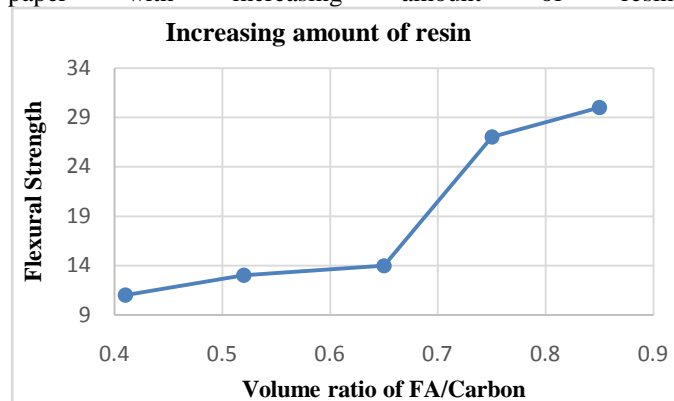


Figure 3(a). Graph showing increasing resistivity of carbon paper with increasing amount of resin.



(a)

Figure 4(a). Graph showing Flexural Strength of carbon paper with increasing amount of resin.

Flexural strength

Increasing amount of resin: Figures shows the variation in the flexural strength & flex modulus of the carbon paper with increase in matrix contents.

The fig. 4(a) shows that the Flexural strength increases with increasing amount of resin. It is observed that the Flexural strength of the paper increases with increasing matrix content from 10 MPa to 32.6 MPa. The result shows that lesser amount of matrix is insufficient to wet or interact with the complete volume of the carbon fiber interface leading to annular gaps at fiber/matrix interface. This is also evident in the optical micrographs of the cross-sectional surface of the composite paper in fig. 4.1 (a) & (b). This results in high porosity in such samples, with no proper load transfer from matrix to fiber, leading to premature failure of the composite paper.

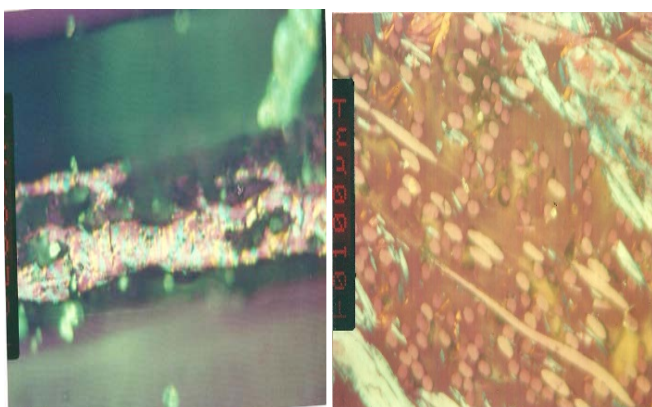
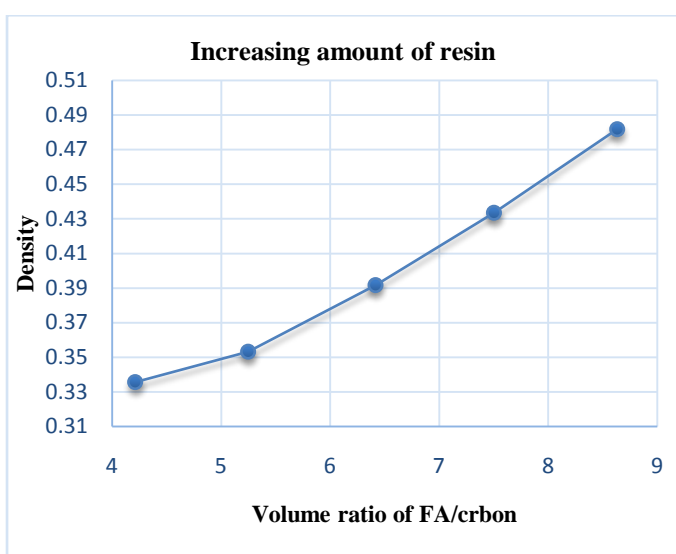


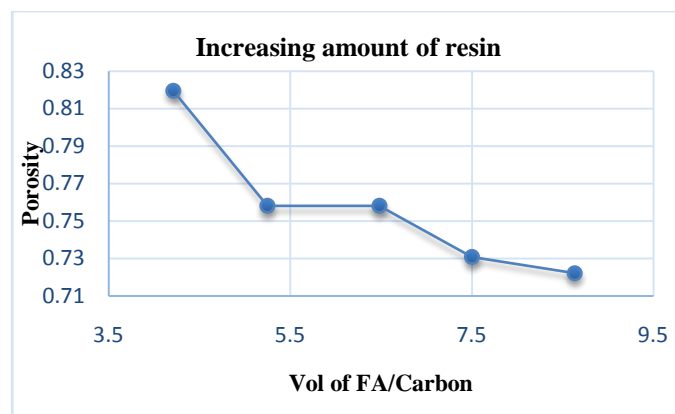
Figure 4.1. Images of optical micrograph (a) with more resin (b) with less resin

Density and Porosity

Increasing amount of resin: Density increases as amount of resin is increased. Pores of carbon paper is filled with resin, similarly porosity is decreased which influences the battery performance (Fig. 5(a)).



(a)



(b)

Figure 5(a) Graph showing density (a) and porosity (b) of carbon paper with increasing amount of resin.

There is an overall shrinkage in the paper with increasing matrix content due to the strong fibre/matrix interactions. This causes an overall decrease in the volume of the paper and hence decreases in the porosity. Hence after wetting the fibre, the excess resin only contributes in filling up the porosity of the composite.

Carbon paper heat treated to different temperatures: The properties of the carbon composite heat treated to different temperatures i.e. 600, 1000 & 2400 °C are tabulated in table 1.

Table 1. Property of carbon paper at different temperatures.

Temp. (°C)	600 °C	1000 °C	2400 °C
Electrical Resistivity (Ω-cm)	0.082±0.022	0.029 ± 0.005	0.003 ± 0.001
	0.082 ± 0.003	0.029 ± 0.004	0.003 ± 0.000
	0.082 ± 0.006	0.029 ± 0.009	0.004 ± 0.001
	0.082 ± 0.020	0.029 ± 0.002	0.004 ± 0.001
Density (g/cc)	0.31 ± 0.02	0.36 ± 0.02	0.38 ± 0.01
	0.31 ± 0.01	0.36 ± 0.01	0.38 ± 0.02
	0.31 ± 0.03	0.36 ± 0.05	0.38 ± 0.02
	0.31 ± 0.06	0.36 ± 0.01	0.38 ± 0.01
Porosity (%)	87.10 ± 1.09	81.87 ± 2.87	72.26 ± 3.67
	87.10 ± 0.48	81.87 ± 1.37	72.26 ± 7.28
	87.10 ± 0.36	81.87 ± 2.37	72.26 ± 5.49
	87.10 ± 2.28	81.87 ± 1.37	72.26 ± 4.87
Flexural Strength (MPa)	3.20 ± 1.15	16.50 ± 5.35	8.74 ± 4.79
	3.20 ± 1.65	16.50 ± 3.27	8.74 ± 3.24
	3.20 ± 0.36	16.50 ± 2.29	8.74 ± 1.17
	3.20 ± 2.25	16.50 ± 7.85	8.74 ± 1.05

Study of electrical resistivity of Carbon paper with increasing heat treatment temperatures (HTT): As shown in table1, the electrical resistivity of the carbon paper decreases with increasing HTT. The decrease in the resistivity

with increasing HTT is due to increase in the degree of graphitization of the matrix at the fiber/matrix interface whereby the structure of the carbon matrix becomes more and more ordered due to stress annealing of the defects at the grain boundaries and increase in the crystallite size. Values as low as 0.003 ohm.cm as been obtained at 2400 °C. This has been further explained by Raman spectroscopy.

Fig. 6 shows the Raman spectra of the carbon paper samples heated to different temperatures dominated by three bands: D (defect/ disorder induced) band, G (graphite like) band, and 2D (second order harmonic to D) band. The intensities of the bands were determined as the area under the spectral curve. The intensity of the G-band (I_G) depends on the structure of the material, incident laser beam intensity, detector characteristics and other parameters. It is therefore used as a reference in determining the relative intensities of the D band (I_D) and 2D band (I_{2D}). The table 2 is showing that the ratio I_D / I_G decreases with increasing HTT. This decrease in the relative intensity of D band signifies long range ordering in the hexagonal lattice owing to the increase in the degree of graphitization with heat treatment.¹⁴

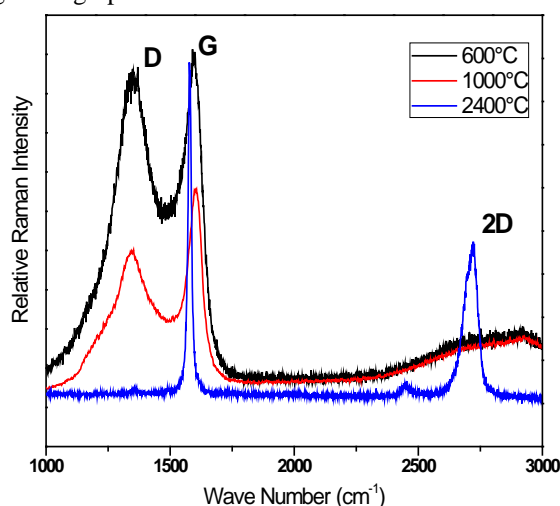


Figure 6. Figure shows the Raman spectra of the carbon paper samples heated to different temperatures.

Table 2. Ratio of I_D / I_G with increasing Temperatures.

HTT	I_D / I_G
600 °C	0.1521
1000 °C	0.9914
2400 °C	0.0634

Moreover the relative intensity of the 2D band also becomes prominent with HTT that signifies long range stacking order in the sample.

The density of the carbon paper increases while the porosity decreases with increasing HTT. This is because of the increase in the fiber/matrix interactions and increased graphitization of the composite sample.

The flexural strength of the paper increases with increase in the HTT from 600°C to 1000°C, probably due to the increase

in the fiber/matrix interactions. The decrease in strength at 2400°C is normal for carbon–carbon composites prepared with non-graphitized carbon fibers. The strong fiber–matrix interactions lead to graphitization of the matrix carbon at the fiber/matrix interface and the failure of the composite is by shear.

Conclusion

A development of carbon composite paper is a two-step process. First is the preparation of carbon paper preform by the well-known paper making technique and second is the composite formation. This can prove as a potential electrode material for Li-ion battery and polymer electrolyte membrane fuel cell. We have demonstrated that by incorporating polyfurfuryl alcohol (PFA) through in situ polymerization of furfuryl alcohol, the performances of commercial electrodes in PEM Fuel Cells were successfully improved. The amount of PFA in the electrode had a significant effect on the properties of the Electrode-PFA Carbon-composite electrodes. The paper is not only conducting also found to have excellent mechanical properties. The composite could thus become important component in the fuel cells for the automobile sector. The nature of carbon fibers, chopped fiber lengths, fiber: matrix ratios and the heat-treatment temperature have been found to be important parameters in controlling the characteristics of an all-carbon composite paper that can be effectively used as an electrode for a fuel cell.

Future Work

Carbon/polymer (Furfuryl Alcohol) composite paper was shown to have excellent properties in terms of porosity, electrical conductivity and flexural strength. Further battery performance will be investigated. Reversible capacity, irreversible capacity, discharge potential will be studied. Number of cycles till it maintains its capacity will be determined. Further its compatibility with various electrolytes can be investigated. Its anode potential and battery capacity will be determined. Its composite with various metals can be made and its influence on battery capacity can be studied. CNT could be impregnated on carbon paper and its battery performance can be studied.

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