

# Properties of Carbon Pastes Prepared with Mixing Ratios of Nano Carbon and Graphite Flakes

Kwangbae Kim and Ohsung Song<sup>†</sup>

Department of Materials Science and Engineering, University of Seoul 163, Seoulsiripdae-ro, Dongdaemum-gu, Seoul 02504, Republic of Korea

(Received July 23, 2018 : Revised September 17, 2018 : Accepted October 17, 2018)

**Abstract** To produce carbon electrodes for use in perovskite solar cells, electrode samples are prepared by mixing various weight ratios of 35 nm nano carbon(NC) and 1  $\mu\text{m}$  graphite flakes(GF), GF/(NC+GF) = 0, 0.5, 0.7, and 1, in chlorobenzene(CB) solvent with a  $\text{ZrO}_2$  binder. The carbon electrodes are fabricated as glass/FTO/carbon electrode devices for microstructure characterization using transmission electron microscopy, optical microscopy, and a field emission scanning electron microscopy. The electrical characterization is performed with a four-point probe and a multi tester. The microstructure characterization shows that an electrode with excellent attachment to the substrate and no surface cracks at weight ratios above 0.5. The electrical characterization results show that the sheet resistance is  $< 70 \Omega/\text{sq}$  and the interface resistance is  $< 70 \Omega$  at weight ratios of 0.5 and 0.7. Therefore, a carbon paste electrode with microstructure and electrical properties similar to those of commercial carbon electrodes is proposed with an appropriate mixing ratio of NC and GF containing a CB solvent and  $\text{ZrO}_2$ .

**Key words** nano carbon, graphite fluke, carbon electrode, chlorobenzene.

## 1. Introduction

Perovskite solar cells(PSCs), which were first reported in 2009, are increasingly drawing attention as a future energy source as they exhibit high energy conversion efficiency(ECE) of approximately 22 %, similar to that of a silicon solar cell, within a short period. Since PSCs can be fabricated through simple solution processing and exhibit high productivity, they are bring active research for commercialization.<sup>1)</sup>

However, PSCs are limited by their large processing costs due to the expensive noble electrode materials. The physical vapor deposition process for electrodes also has require long process time and cost. To solve these problems, replacing noble materials with non-metal materials that do not require vacuum processing is being actively researched using low-cost metals including  $\text{MoO}_x$ - $\text{Al}^{2)}$  or conducting polymers such as polyaniline.<sup>3)</sup>

Many studies regarding the replacement of expensive noble materials, such as Au and Ag, and organic-hole transport layer with carbon paste have been recently reported. Zhou et al.<sup>4)</sup> fabricated a carbon paste electrode

by mixing a conductive carbon extracted from commercial carbon paste, in chlorobenzene(CB) solvent and  $\text{ZrO}_2$ . They reported a PSC with 9 % ECE using their prepared carbon paste. Zhang et al.<sup>5)</sup> fabricated a carbon paste electrode using terpineol and reported an 11 % ECE using this material. Mei et al.<sup>6)</sup> reported 12.8 % ECE using a carbon paste electrode and Zhang et al.<sup>7)</sup> fabricated a glass/FTO/ $\text{TiO}_2$ /Pervoskite carbon device using commercial carbon paste and reported a maximum ECE of 8.31 %.

However, in these reports, even if the carbon paste was fabricated with the same carbon material, the material easily formed flakes or surface cracks during the drying process, causing poor reproducibility due to the deterioration of electrical conduction. The reproducibility issue of carbon paste is greatly dependent on the size, shape, and mixing ratio of the constituent carbon particles. In addition, a solvent that does not react with the under layers must be selected. Various additives, including a binder with an appropriate band gap and that binds carbon particles, must be added to improve the ECE of the device for good reproduction.

However, since the contents of the commercial carbon

<sup>†</sup>Corresponding author

E-Mail : [songos@uos.ac.kr](mailto:songos@uos.ac.kr) (O. Song, Univ. of Seoul)

© Materials Research Society of Korea, All rights reserved.

This is an Open-Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

paste are not disclosed for proprietary reasons, only the same commercial carbon paste must be used continuously for reproducibility. Even carbon paste directly fabricated by some research groups often do not have the accurate details regarding the carbon size, solvent, and binder. Thus, it is difficult to obtain reproducible results.

Therefore, this study used nanocarbon(NC) and graphite flake(GF), whose size and shape data are known, and compared with the commercial carbon paste employed by Hashmi et al.<sup>8)</sup> For the solvent, chlorobenzene(CB) that has no reactivity with the perovskite layer was used. For the binder, this study employed a small quantity of  $ZrO_2$ .

## 2. Experimental Procedure

In this study, the particle size of the NC(Denka Ltd.) and GF(KLK Ltd.) used in the production of the carbon paste was confirmed using a transmission electron microscopy(TEM, JEM 2100F, JEOL Ltd.). For TEM analysis, solutions of NC and GF were diluted in ethanol, dried on a mesh grid, and subsequently analyzed. As shown in Fig. 1, the particle sizes of the sphere type NC and flat type GF were 35 nm and 1  $\mu m$ , respectively.

As shown in Table 1, the NC and GF were mixed to a total weight of 1 g and four carbon pastes were fabricated with various weights of GF. Each carbon paste was fabricated by mixing the carbon body mixed at different ratios of GF/(NC+GF) with the  $ZrO_2$  binder and CB, which is unreactive with the perovskite layer, followed by ball-milling at 350 rpm for 6 hours.

For sample A, the carbon paste was fabricated by mixing 1 g of NC, 15 mL of CB, and the 0.08 g  $ZrO_2$  binder. For sample B, sample C, and sample D were prepared as described in Table 1.

To compare the properties of the fabricated carbon pastes with those of commercial carbon electrodes (CCEs), CCE\_K(carbon paste, KLK Ltd.; Korea) and CCE\_S(Elcocarb B/SP, solaronix Ltd.; Swiss) were prepared. CCE\_K was prepared using a mixture of NC, GF and 2-ethoxyethanol as a solvent. For CCE\_S, the com-

ponents of the carbon paste were unknown, but Hashmi et al.<sup>8)</sup> reported that it could be successfully used for the fabrication of a PSC device.

Fig. 2 shows a schematic of the device used for analysis of electrical properties. On a substrate with a 5 mm wide FTO etching part at the center of  $25 \times 25$  mm<sup>2</sup> glass/FTO, the prepared carbon paste sample was coated in a  $10 \times 16$  mm<sup>2</sup> rectangular shape using the doctor blade method and subsequently dried at 100 °C for 30 min to obtain the final structure in Fig. 2(a). Fig. 2(b) shows the cross-sectional image that was cut along the center line shown in Fig. 2(a).

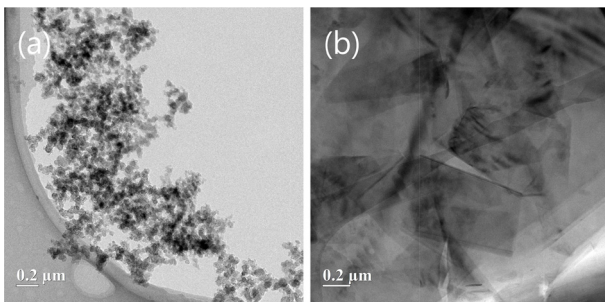
Finally, for the two-point measurement, as shown in Fig. 2, the resistance( $R_{\text{carbon}}$ ) of the carbon electrode and interfacial resistance( $R_{\text{FTO/carbon}}$ ) were measured. In addition, the microstructure in the rectangular dotted line of the carbon electrode sample in Fig. 2(a) was analyzed via optical microscopy(GIA Ltd.) and field emission scanning electron microscopy(FE-SEM, S-4300, Hitachi Ltd.).

To confirm the sheet resistance of the fabricated carbon electrode, the section marked with a white dotted line in Fig. 2(a) was measured five times using a four-point probe(CMT-SR1000N, AIT) and the average value was taken as the sheet resistance.

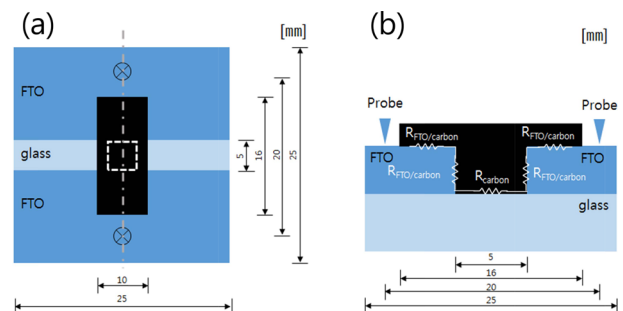
The resistances of the carbon electrodes and substrates were measured using a multimeter(117 Multimeter, Fluke Ltd.) with the probe contacting two points in the section separated by a straight distance of 20 mm. Thus,  $R_T$  of

**Table 1.** Carbon paste sample description.

Sample	NC [g]	GF [g]	$ZrO_2$ [g]	Chlorobenzene [mL]
A	1	0	0.08	15
B	0.5	0.5	0.08	15
C	0.3	0.7	0.08	15
D	0	1	0.08	15
CCE_K	unknown(2-Ethoxyethanol)			
CCE_S	unknown			



**Fig. 1.** TEM images of (a) NC and (b) GF.



**Fig. 2.** Illustration of the simplified sample ; (a) planar view and (b) cross sectional view.

$R_T = R_{\text{carbon}} + 2(R_{1\text{FTO}/\text{carbon}} + R_{2\text{FTO}/\text{carbon}})$  was measured to indirectly confirm  $R_1$  and  $R_2$ .

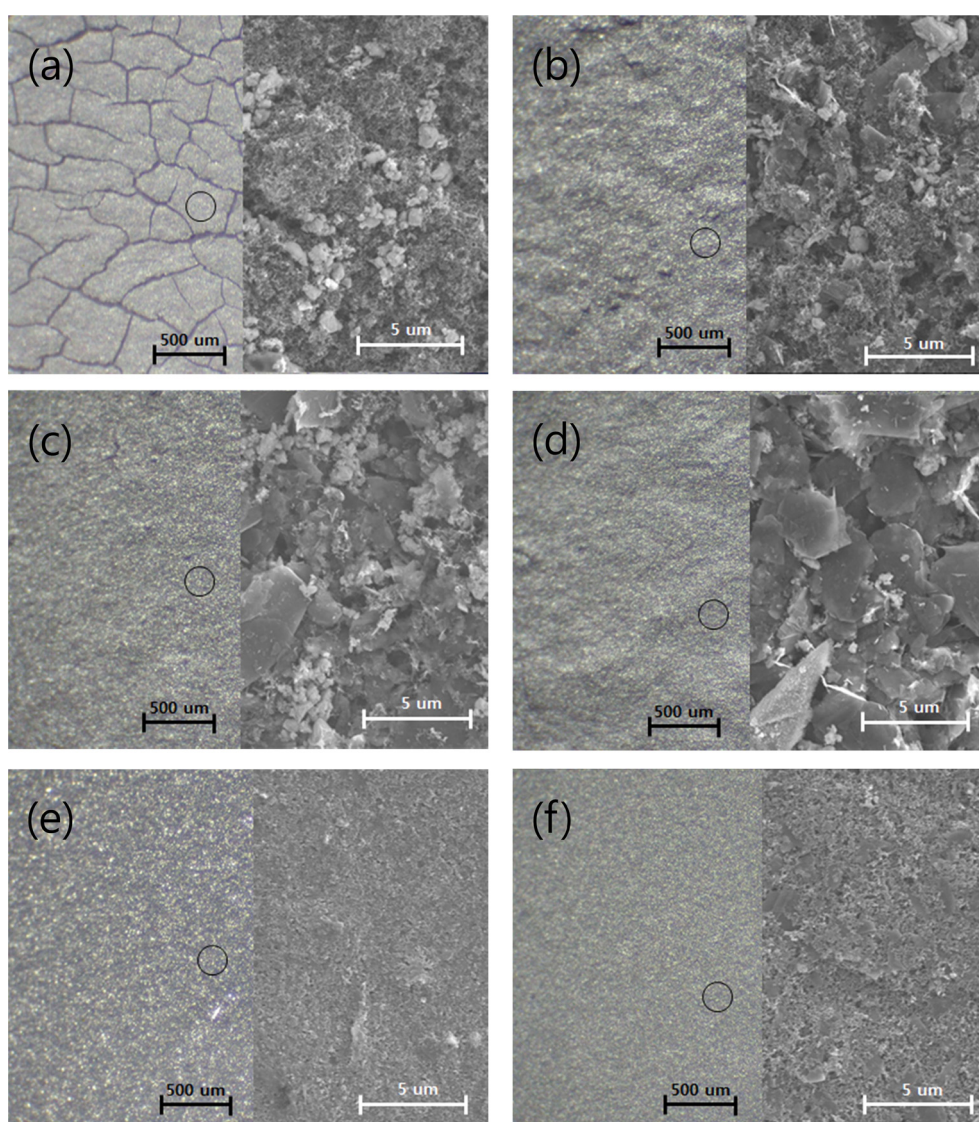
### 3. Result and Discussion

Fig. 3 shows the optical microscopy(left side) and FE-SEM surface image(right side) of the prepared carbon electrode.

Fig. 3(a) shows an image of the carbon electrode composed of only NC(sample A). Macro cracks were confirmed in the optical microscopy image on the left side of Fig. 3(a). Cracks with a width of  $30\ \mu\text{m}$  along a length of approximately  $300\ \mu\text{m}$  were observed over the entire surface. Because of these cracks, detachment caused by a weak electrode structure and increased interfacial

resistance due to the increased sheet resistance were expected. Aggregation of the NC particles due to the high cohesive force after solvent evaporation in the drying process was likely the cause of these cracks.<sup>9)</sup> This is consistent with the NC aggregation confirmed in previous reports. Furthermore, an enlarged FE-SEM image of the section marked with a black circle in the left image is shown on the right side, confirming that it was composed of only NC as intended.

Fig. 3(b) shows the microstructure of carbon electrode fabricated using sample B(0.5 g of NC and GF). The optical microscopy image on the left side showed a surface without cracks, unlike the sample shown in Fig. 3(a). As the GF with a relatively large particle size was added, it connected the NC aggregations, preventing the



**Fig. 3.** Optical(left-side) and FE-SEM(right-side) images of GF/(NC+GF) the carbon pastes of (a) 0, (b) 0.5, (c) 0.7, (d) 1, (e) CCE\_K, and (f) CCE\_S.

**Table 2.** Sheet resistances of the prepared carbon electrodes.

Sample	Top [ $\Omega/\text{sq}$ ]	Center [ $\Omega/\text{sq}$ ]	Bottom [ $\Omega/\text{sq}$ ]	Right [ $\Omega/\text{sq}$ ]	Left [ $\Omega/\text{sq}$ ]	Average [ $\Omega/\text{sq}$ ]
A	3779	2128	4389	1789	1961	2,809.2
B	56	53	48	51	54	52.4
C	65	64	69	66	67	66.2
D	75	61	81	113	76	81.2
CCE_K	31	29	33	29	27	29.8
CCE_S	26	27	29	25	26	26.6

formation of cracks. The FE-SEM image on the right side confirmed that NC and GF were mixed in a 1:1 ratio as intended.

Fig. 3(c) shows the microstructure of the carbon electrode fabricated with sample C (0.3 g of NC and 0.7 g of GF). The optical microscopy image on the left side showed a flatter surface compared to Fig. 3(b). This was likely due to the increased ratio of GF with flat shaped particles, as confirmed by TEM. The FE-SEM image on the right side confirmed that NC and GF were mixed in a 1:2.3 ratio.

Fig. 3(d) shows the image of the carbon electrode fabricated with sample D, which was composed of only GF. The optical microscopy image on the left side confirmed a flat surface, similar to that observed in Fig. 3(c). This was likely because the material was composed solely of flat type GF, as confirmed by TEM. The FE-SEM image on the right side confirmed that the surface microstructure is composed of solely GF as intended.

Fig. 3(e) shows the microstructure of the CCE\_K sample. The optical microscopy image on the left side showed a flat surface without cracks. The FE-SEM image on the right side showed a uniform surface composed of micro carbon particles.

Fig. 3(f) shows the microstructure of the CCE\_S sample. The optical microscopy image on the left side showed a flat surface with no cracks. Similar to Fig. 3(e), the FE-SEM image on the right side showed a surface composed of micro carbon particles.

Therefore, the carbon paste electrode fabricated by mixing NC, GF, CB solvent, and  $\text{ZrO}_2$  binder exhibited poor surface uniformity compared to the commercial carbon paste electrode, but it was possible to fabricate a carbon electrode without cracks.

Table 2 shows the sheet resistance analysis of the carbon paste samples. Samples A and B showed sheet resistances of 2,809.2 and 52.4  $\Omega/\text{sq}$ , respectively, with the resistance of sample B approximately 50 times smaller compared to that of sample A. Furthermore, the optimum sheet resistances of 66.2 and 81.2  $\Omega/\text{sq}$  were obtained for sample C (GF 70 %) and sample D (GF 100 %), respectively.

In contrast, the commercial carbon pastes CCE\_K and

**Table 3.** Interfacial resistance result.

Sample	Interfacial Resistance ( $\Omega$ )
A	36,000
B	52
C	63
D	85
CCE_K	18
CCE_S	18

CCE\_S showed optimum sheet resistances of 29.8 and 26.6  $\Omega/\text{sq}$ , respectively, which are 50 % smaller than that of sample B. This is likely because, as confirmed in the microstructure images, the number of conductive channels of NC and GF decreased due to the microporous structure and the sheet resistance increased from the addition of the  $\text{ZrO}_2$  binder. Nevertheless, a sheet resistance of 50-60  $\Omega/\text{sq}$  is considered to be usable for electrodes in PSCs.

Table 3 shows the interfacial resistance analysis of the device using the model in Fig. 2(b). For the proposed resistance model, the contact resistance between the probe and FTO was assumed to be zero. The total interfacial resistance can be expressed as  $R_T = R_{\text{carbon}} + 2(R_{1\text{FTO}/\text{carbon}} + R_{2\text{FTO}/\text{carbon}})$  and the measured interfacial resistances of the samples are listed in Table 3.

For sample A which, was fabricated using only NC, the interfacial resistance was the highest at 36,000  $\Omega$ . This is considered to be caused by the decreased channeling in the carbon electrode due to cracks in microstructure, which increased sheet resistance. The disconnected part at the interface also increased, further increasing the interfacial resistance.

For sample B with a GF mixture ratio of 50 %, a interfacial resistance of approximately 50  $\Omega$  was obtained. It showed electrical properties that can be employed for a very low interfacial resistance electrode compared to sample A. Electrical conductivity was enhanced as spaces between the flat type GF were filled with spherical NC.

For sample C with a GF mixture ratio of 70 %, a interfacial resistance of approximately 60  $\Omega$  was obtained, which is consistent with the change of the sheet re-

sistance described above. The reason of increase in resistivity according to increase in the amount of additive GF is because of decrease in contacting area between the flat type GF and concavo-convex shaped FTO layer at the bottom.

For sample D fabricated only with GF, a interfacial resistance of  $85 \Omega$  was obtained, which is slightly higher than those of samples B and C, and agreed with the previously measured sheet resistance. This interfacial resistance ( $\geq 80 \Omega$ ) is expected to be inappropriate for use as an electrode.

For the CCE\_K and CCE\_S samples, a very low interfacial resistance of  $18 \Omega$  was obtained and was lower than the sheet resistance. This was likely due to the microstructure described above where the surface was uniformly coated and uniform channeling of carbon particles was observed.

Therefore, for the carbon electrode fabricated with sample B (GF mixing ratio of 50 %), a relatively low sheet resistance and interfacial resistance of approximately  $50 \Omega$  was obtained. Thus, the result implies that the proposed appropriate NC and GF mixed carbon paste in CB and  $ZrO_2$  for electrode shows feasible resistance compared to that of commercial carbon pastes.

#### 4. Conclusion

In this study, carbon paste electrodes were prepared by mixing 35 nm NC and  $1 \mu\text{m}$  GF with CB solvent and  $ZrO_2$  binder to form a simple device that can confirm microstructure and interfacial resistance. Analysis of the microstructure of the fabricated carbon electrodes showed surface cracks in sample A fabricated with only NC, and flat surfaces with no cracks in samples B, C, and D fabricated with 50 %, 70 %, and 100 % GF, respectively, similar to those of the commercial paste samples. In terms of electrical properties, sample B (GF 50 %) showed a low resistance of approximately  $50 \Omega$ , which is higher

than those of commercial carbon paste. However, sample B could still be used as a PSC electrode, because its resistance fell below the threshold required for PSCs. Therefore, this study confirmed the possibility of employing our proposed carbon pastes of mixing NC and GF at an appropriate weight ratio with CB solvent and  $ZrO_2$  binder for carbon electrodes in PSCs.

#### Acknowledgement

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2017-R1D1A1B03029347)

#### References

1. A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *J. Am. Chem. Soc.*, **131**, 6050 (2009).
2. Y. X. Zhao, A. M. Nardes and K. Zhu, *Appl. Phys. Lett.*, **104**, 213906 (2014).
3. B. He, Q. Tang, T. Liang and Q. Li, *J. Mater. Chem. A*, **2**, 3119 (2014).
4. H. Zhou, Y. Shi, Q. Dong, H. Zhang, Y. Xing, K. Wang, Y. Du, T. Ma, *J. Phys. Chem. Lett.*, **5**, 3241 (2014).
5. L. Zhang, T. Liu, L. Liu, M. Hu, Y. Yang, A. Mei and H. Han, *J. Mater. Chem. A*, **3**, 1965 (2015).
6. A. Mei, X. Li, L. Liu, Z. Ku, T. Liu, Y. Rong, M. Xu, M. Hu, J. Chen, Y. Yang and H. Han, *Science*, **345**, 295 (2014).
7. F. Zhang, X. Yang, H. Wang, M. Wang, M. Cheng, J. Zhao and L. Sun, *ACS Appl. Mater. Interfaces*, **6**, 16140 (2014).
8. S. G. Hashmi, D. Martineau, M. I. Dar, Teemu T. T. Myllymaki, T. Srikka, V. Ulla, S. M. Zakeeruddin and M. Gratzel, *J. Mater. Chem. A*, **5**, 12060 (2017).
9. B. V. Scarnato, S. Vahidnia, D. T. Richard and T. W. Kirchstetter, *Atmos. Chem. Phys.*, **13**, 5089 (2013).