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CENTRIFUGAL CARBON COATING OF ELECTROSPINNING SYNTHESIZED GRAPHITE SUBSTRATES: EFFECT OF PROCESS CONDITIONS ON COATING QUALITY

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In this work, Graphite samples have been coated via centrifugal method in various conditions. Poly methyl methacrylate has been used as the binder and after a suitable heat treatment and resin removal, a stick adhesive layer was formed. Using SEM and TGA techniques, effect of centrifugal rotation speed, resin to particles ratio and heat treatment procedure were studied on coating conditions. The best morphology and highest coating density were obtained at centrifugal rotation speed = 5000 rpm, resin to particles weight ratio of 0.05 and a two-stage heat treatment at 100 and 300^{o}C.

Keywords: Graphite, Carbon Nanoparticles, Poly Methyl Methacrylate

1. Introduction

Due to the various applications of the carbon coatings at diverse high temperature fields, researchers have been struggling with the synthesis and application of these materials in the recent years [1-3]. The main limitation of these coatings is their low oxidative resistance, especially at high temperatures. So, different Carbon types such as functional graded materials (FGMs) containing Si or B atoms have been vastly developed. Among various conventional Carbon coating procedures such as electrophoretic deposition [4-7], centrifugal coating [8-12], screen printing [13, 14] and spraying [15], electrophoretic coating is used frequently due to its advantages. However, coating density is relatively low in this method comparing to centrifugal and spraying approach. Besides, a very smooth and high density initial surface is required for this method. As many industrial samples have a relative rough surfaces, this technique cannot be used directly and some pre-coating methods is required to be used such as centrifugal coating.

In this work, porous Graphite samples synthesized via electrospinning method, have been coated using centrifugal forces. This method has been applied for phosphor deposition previously [8], but it has not been used for carbon coating yet. In this method, stable suspension containing carbon nanoparticles or

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nanotubes and a suitable polymeric resin, Poly methyl methacrylate (PMMA), in cyclohexane solution were centrifuged in a tube; meanwhile the graphite sample was located and fixed in one side of centrifuge tube. So, a smooth controllable high density carbon layer formed on the external surface of Graphite sample. After a suitable heat treatment and resin removal under a compact force, a relatively stick adhesive layer was formed. Effect of centrifugal rotation speed (CRS), resin to particle ratio and heat treatment procedure were investigated on coating thickness and quality.

2. Experimental procedure

2.1. Sample preparation

Graphite samples with 1 cm^2 surface were inserted and fixed in centrifuge tubes containing 3 cc suspensions of carbon nanoparticles and PMMA in cyclohexane. Suspension concentration was equal to 50 mgC/cc and PMMA /carbon weigh ratio was equal to 0.05. These suspensions were centrifuged 3 min at 2000 rpm, and then the graphite samples were dried in 300^{o}C oven for 60 minutes for drying and resin removal (PMMA boiling point equals to 200^{o}C). In order to investigate effect of process conditions on coating thickness and quality the above-mentioned procedure was repeated in centrifugal rotation speeds of 3000, 4000 and 5000 rpm, PMMA /carbon weigh ratios of 0.15, 0.25 and 0.4, and a two-stage heat treatment procedure (30 min at 100^{o}C and 30 min at 300^{o}C). The detailed process conditions are listed in Table 1.

2.2. Characterization

Scanning Electron Microscopy (SEM) was performed using Philips XL 30 instrument to investigate coating thickness and morphology. Thermal Gravimetric Analysis (TGA) procedure was employed using a controlled-atmosphere oven and a digital electronic balance (accuracy 0.0001g) to track samples' weight changes.

Table 1

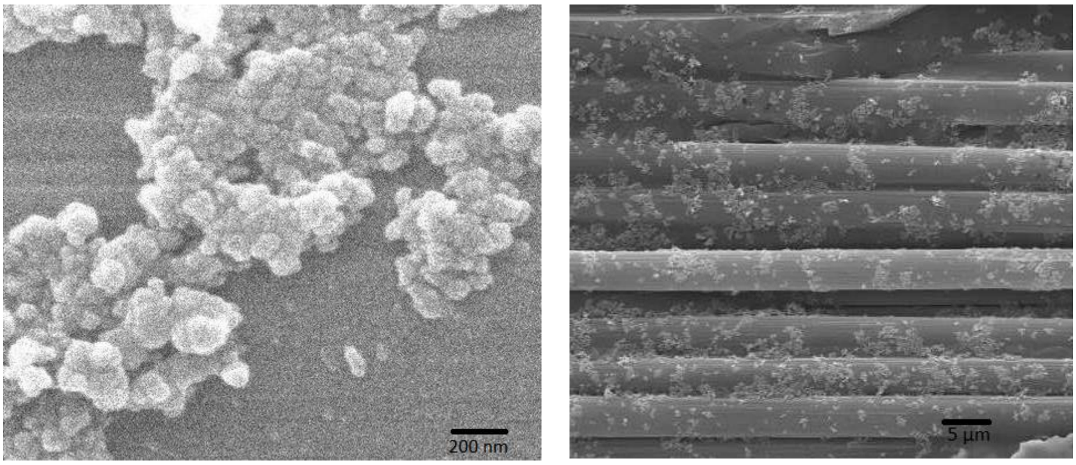
Process conditions of centrifugal coating method and coating layer properties [1]

Sample	CRS [2] (rpm)	PMMA to Carbon weight ratio	Heat Treatment	Coating Weight (mg) [3]	Coating Thickness (μm) [4]	PMMA Weight%	Water %	Density (gr/cm^3)	%Relative density [5]
A1	2000	0.05	Two-stage [6]	80.1	468	1.6	3.2	1.63	71.9
A2	3000	0.05	Two-stage	49.5	240	1.8	3.3	1.96	86.5
A3	4000	0.05	Two-stage	11.7	54	1.53	3.5	2.05	90.9
A4	5000	0.05	Two-stage	9.8	44	1.51	3.3	2.12	93.7
A5	5000	0.05	One-stage [7]	-	-	-	-	-	-
A6	5000	0.05	One-stage [8]	-	-	-	-	-	-
A7	5000	0.15	Two-stage	-	-	-	-	-	-
A8	5000	0.25	Two-stage	-	-	-	-	-	-
A9	5000	0.4	Two-stage	-	-	-	-	-	-

1- Because of undesired SEM results and non-homogeneous coating layer thickness, thickness measurement and density calculations did not performed for samples A5 to A9
2- centrifugal rotation speed
3- Coating weight before heat treatment
4- From SEM images
5- Respect to pure bulk carbon
6- 30 min at 100°C and 30 min at 300°C
7- 60 min at 300°C
8- 60 min at 100°C

3. Results and discussion

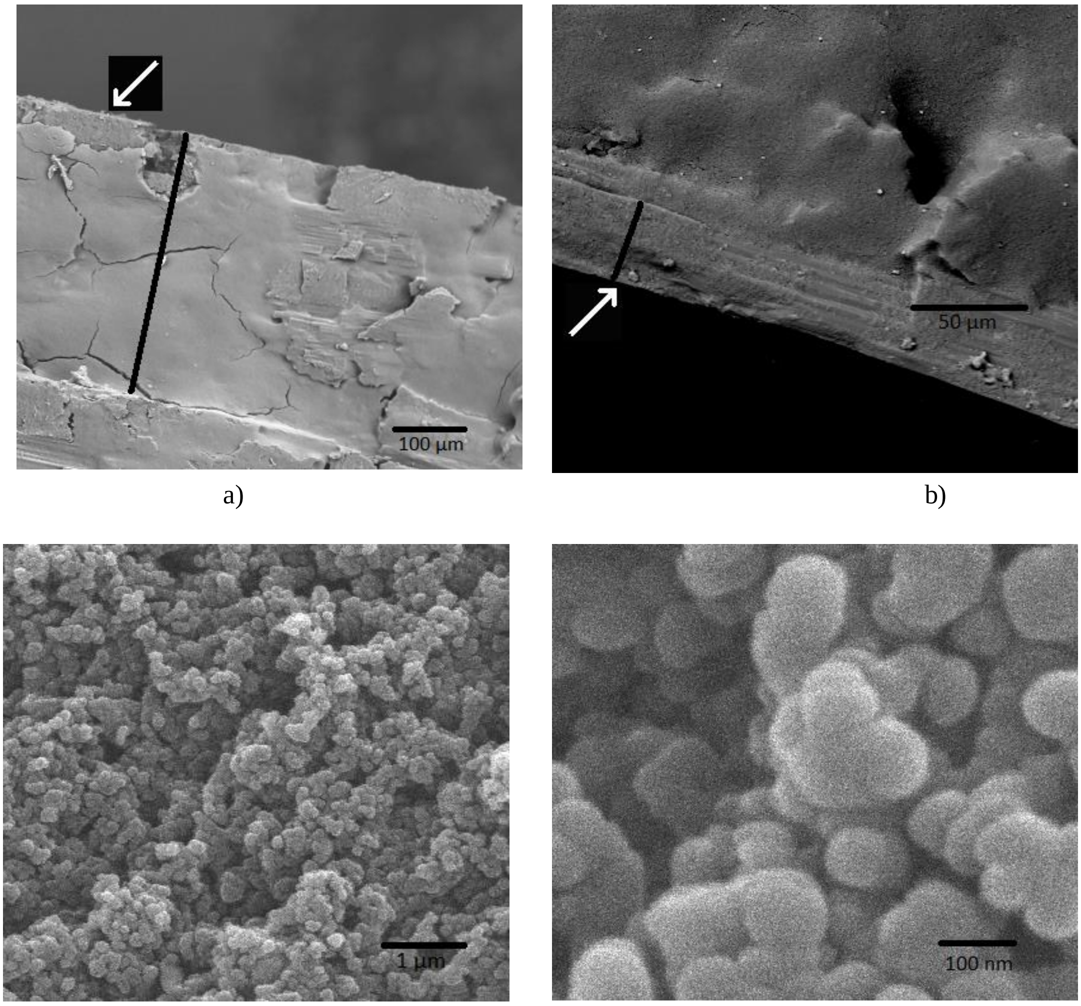
SEM images of sample A0, the initial uncoated electrospinning synthesized sample, are presented in Figs. 1-a and 1-b. Some 5 µm width carbon fibers are seen in this image beside 50-150 nm carbon particles. This unpacked low density layer structure is not suitable for conventional electrophoretic coating procedures.



a) b)

Fig. 1- SEM image of sample A0, initial electrospinning synthesized sample, a) Scale bar = 200 nm, b) Scale bar = 5 µm.

Experimental conditions and properties of the samples A1, A2, A3 and A4, synthesized at different CRSs are listed in Table 1. SEM images of samples A1 and A4 centrifugally coated at CRSs 2000 and 5000 rpm are presented in Fig. 2. As seen in these images, coating thickness is decreased by increasing CRS. On the other hand, coating layer density is increased by increasing CRS (table 1). Coating layer density was determined using the SEM and TGA results, revealing coating thickness and mass, respectively. This can be explained by this fact that as CRS increases from 2000 to 5000 rpm, centrifugal force raises and subsequently a rather high density coating is formed. A rather porous low density coating is formed in low CRSs (Samples A1 and A2). On the other hand, in high amounts of CRS, a large fraction of carbon particles would tend to scatter due to the extreme agitation and settle on the centrifuge machine tube wall instead of samples' surface and consequently, the coating layer weight will be less than low CRSs (Table 1).

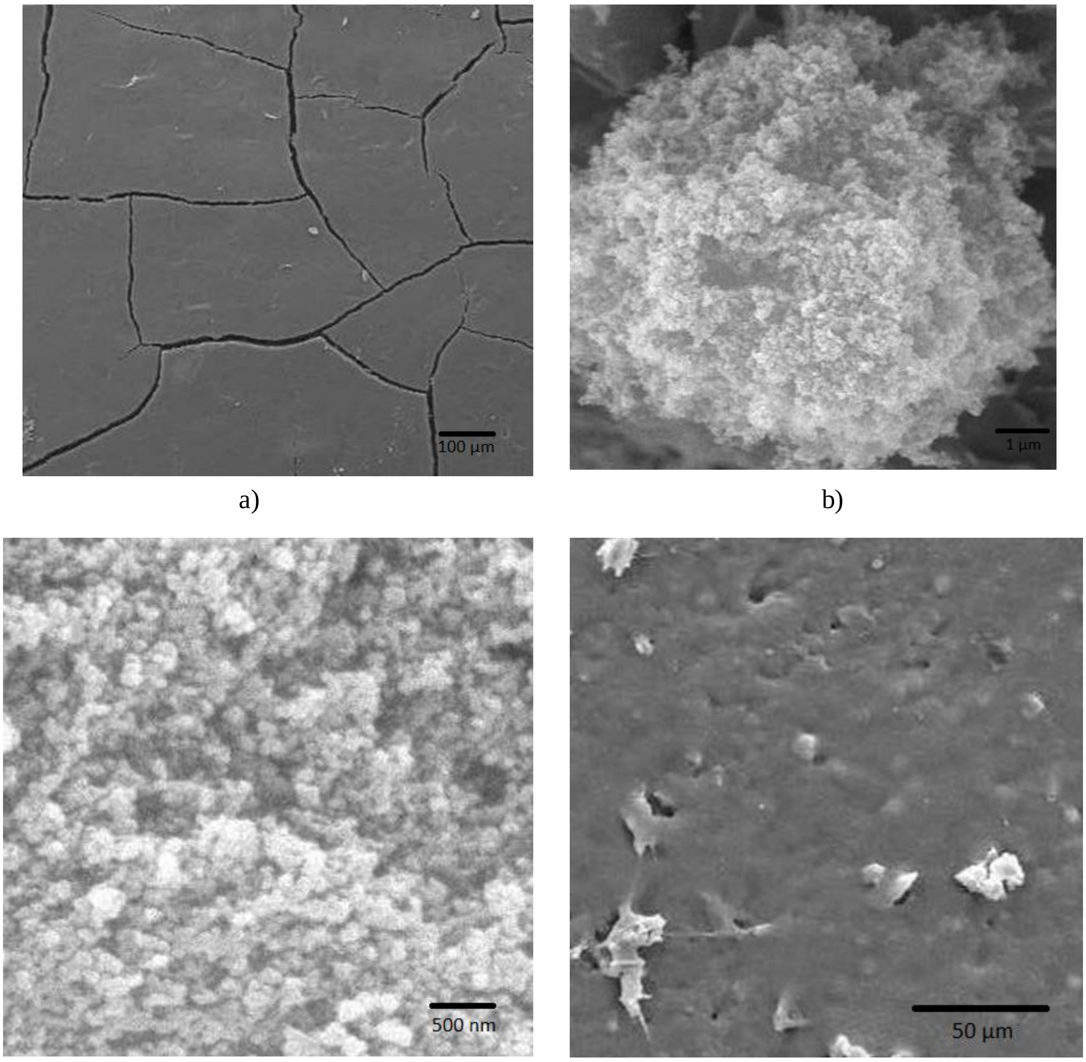


a) b)

c) d)

Fig. 2- SEM image of sample a) A1: centrifugal coated at 2000 rpm, b) A4: centrifugal coated at 5000 rpm, Scale bar = 50 µm, c) A4: centrifugal coated at 5000 rpm, Scale bar = 1, µm d) A4: centrifugal coated at 5000 rpm, Scale bar = 100 nm.

Fig. 3 presents coating morphology of samples at different heat treatment procedures. Using one-stage heat treatment at 300 ^{o}C instead of two-stage heat treatment led to formation of surface cracks and porosities due to quick removal of water and PMMAsimultaneously from samples' surface (Fig. 3-a, sample A5). These cracks are not seen in samples A1 to A4 with two-stage heat treatment. Some residual PMMA agglomerates are seen in Fig. 3-a. PMMA agglomerates' structure is shown in SEM images 3-b and 3-c, including some nanometric PMMA particles. On the other hand, heating sample up to 100^{o}C hold more residual PMMA agglomerates in coating layer without any surface cracks (Fig. 3-d, sample A6).

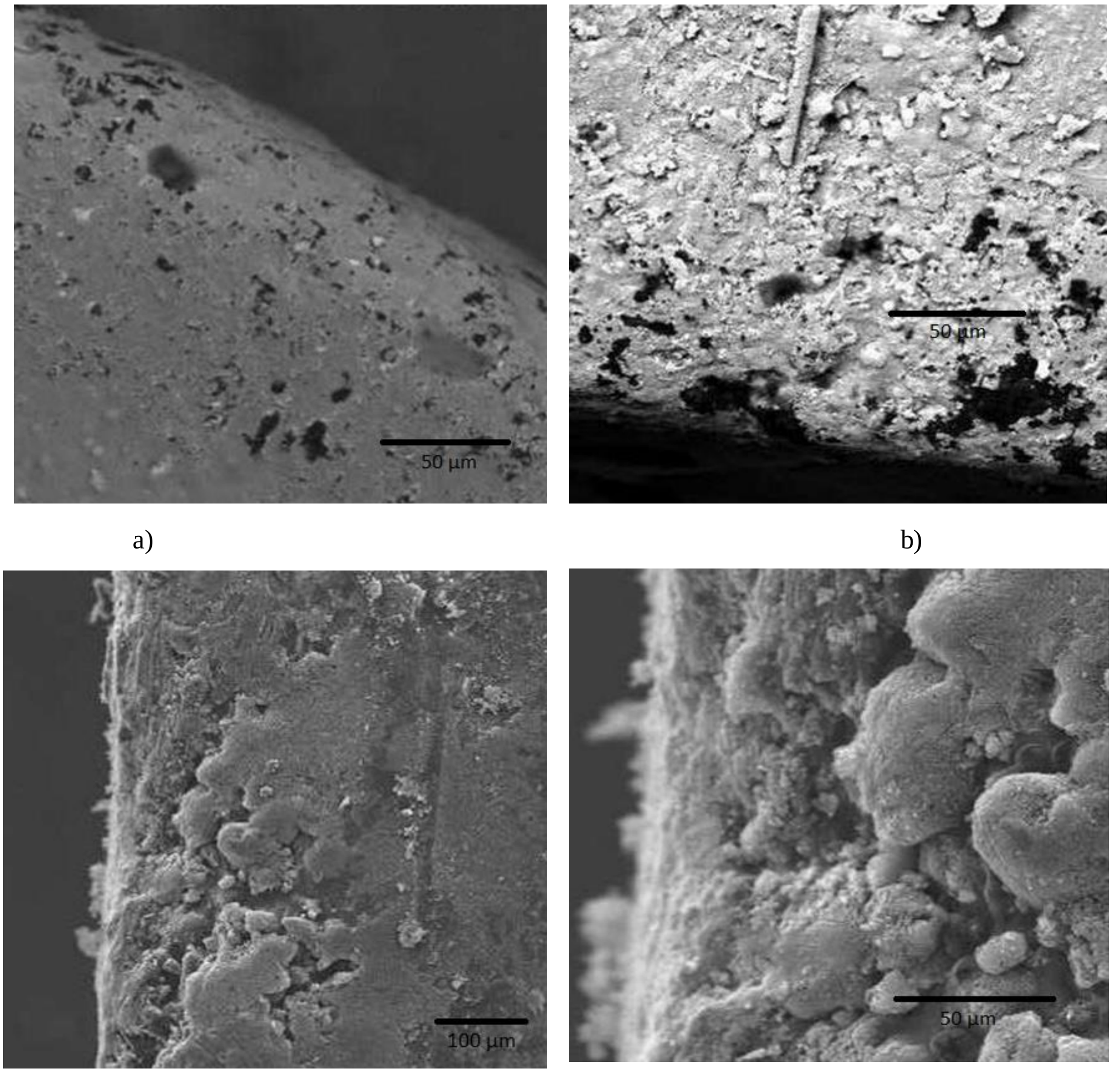


a) b)

c) d)

Fig. 3- SEM image of: a-c) sample A5 in three magnifications, and d) sample A6 (Table 1)

SEM images of samples with different PMMA/carbon weight ratios are presented in Fig. 4. As seen in these images, huge porosities and cracks are formed in coating layer due to large amount of PMMA evaporated and removed from samples' surface. So, coating density is decreased dramatically by increasing PMMA/carbon weight ratio (Table 1, samples A7 to A9).



a) b)

c) d)

Fig. 4- SEM image of a) sample A7, b) sample A8, c) sample A9, Scale bar = 100 µm and d) sample A9, Scale bar = 50 µm (Table 1).

Samples' coating density was calculated using SEM and TGA results. As the samples' initial surface area equals to 1 cm^2, coating volume can be calculated easily from coating thickness (Table 1). Thus, coating density can be determined by dividing final coating weight (after heat treatment) to this amount. These results are listed in table 1 for samples A1 to A4.

4. Conclusion

Centrifugal coating process is described and employed in this study as an effective technique to produce high density smooth carbon coating layer on the surface of electrospinning synthesized samples. The optimum conditions led to a 44 µm carbon coating layer with relative density of %93.7. Increasing centrifugal rotation speed, decreasing PMMA to carbon weight ration and using two-stage heat treatment led to decreasing coating layer thickness and increasing its density. It seems that this method can be used for similar applications, which an initial rough surface would be coated to produce a smooth coating layer.

REFERENCES

[1]. *X. Fan and D. Diao*, "The adhesion behavior of carbon coating studied by re-indentation during in situ TEM nanoindentation", in Appl. Surf. Sci., **vol. 362**, 2016, pp. 49-55.

[2]. *C. S. Sujith Kumar, S. Suresh, L. Yang, Q. Yang and S. Aravind*, "Flow boiling heat transfer enhancement using carbon nanotube coatings", in Appl. Therm. Eng., **vol. 65**, 2014, pp. 166-175.

[3]. *A. Ponrouch, A. R. Goni, M. T. Sougrati, M. Ati, J. Tarascon, J. Nava-Avendano and M. R. Palacin,* "A new room temperature and solvent free carbon coating procedure for battery electrode materials", in Energy Environ. Sci., **vol. 6**, 2013, pp. 3363-3371.

[4]. *A. Boccaccini and I. Zhitomirsky*, "Application of electrophoretic and electrolytic deposition techniques in ceramics processing", in Curr. Opin. Solid State Mater. Sci., **vol. 6**, 2002, pp. 251-260.

[5]. *Y. Solomentsev, S. A. Guelcher, M. Bevan and J. L. Anderson.*, "Aggregation dynamics for two particles during electrophoretic deposition under steady fields", in Langmuir, **vol. 16**, 2000, pp. 9208–9216.

[6]. *A. Boccaccini, J. Cho, T. Subhani, C. Kaya and F. Kaya*, "Electrophoretic deposition of carbon nanotube–ceramic nanocomposites", in J. Eur. Ceram. Soc., **vol. 30**, 2010, pp. 1115–1129.

[7]. *J. Maria, C. Alberto, C. Francisco, Q. Nancy and R. Aldo*, "Electrophoretic Codeposition of $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and Carbon Nanotubes for Developing Composite Cathodes for Intermediate Temperature Solid Oxide Fuel Cells", in Int. J. Appl. Ceram. Technol., **vol. 7**, 2010, pp. 30–40.

[8]. *A. Ozols, M. Barreiro, E. Forlerer and H. R. Sirkin*, "Coating of Co–Cr–Mo alloy for surgical implants by centrifugal spray: Preliminary evaluation", in Surf. Coat. Technol., **vol. 200**, 2006, pp. 5884-5888.

[9]. *H. Tong, L. B. Kong and C. M. Wang*, "Electroless deposition of Ag onto p-Si(100) surface under the condition of the centrifugal fields", in Thin Solid Films, **vol. 496**, 2006, pp. 360-363.

[10]. *M. Atobe, A. Murotani, S. Hitose, Y. Suda, M. Sekido, T. Fuchigami, A. Chowdhury and T. Nonaka*, "Anodic polymerization of aromatic compounds in centrifugal fields", in Electrochim. Acta, **vol. 50**, 2004, pp. 977-984.

[11]. *P. V. Liedekerke, E. Tijskens, E. Dintwa, F. Rioual, J. Vangeyte and H. Ramon*, "DEM simulations of the particle flow on a centrifugal fertilizer spreader", in Powder Technol., **vol. 190**, 2009, pp. 348-360.

[12]. *U. Schaflinger*, " Centrifugal separation of a mixture", in Fluid Dyn. Res., **vol 6**, 1990, pp. 213-249.

[13]. *T. M. Lee, Y. J. Choi, S. Y. Nam, C. W. You, D. Y. Na and H. C. Choi*, "Color filter patterned by screen printing", in Thin Solid Films, **vol. 516**, 2008, pp. 7875-7880.

[14]. *D. Erath, A. Filipović, M. Retzlaff, A. K. Goetz, F. Clement, D. Biro and R. Preu*, " Advanced screen printing technique for high definition front side metallization of crystalline silicon solar cells", in Sol. Energ. Mat. Sol. C., **vol. 94**, 2010, pp. 57-61.

[15]. *J. Wu, J. Yang, H. Fang, S. Yoon and C. Lee,* "The bond strength of Al–Si coating on mild steel by kinetic spraying deposition", in Appl. Surf. Sci., **vol. 252**, 2006, pp. 7809-7814.