EFFECT OF STRUCTURAL CHANGES ON ORR REACTIVITY OF N-DOPED CARBONIZED SUGI WOOD

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Introduction

The application of carbon materials to fuel cells may contribute to CO_2 reduction and provide a method to retain a hydrogen economy in a low carbon society. The fuel cell as a power source has more advantages in terms of CO_2 emission than energy from biomass. Among fuel cells the polymer electrolyte fuel cell (PEFC) is a promising power source. If fuel cells are developed from biomass, ideal electrodes with less environmental impact on the final disposal process will be established.

Nitrogen-doped carbon-based catalysts have been recognized as promising non-precious metal catalysts for polymer electrolyte fuel cells [1, 2]. If the carbon is used from biomass such as wood it is more environmentally friendly and expands the possibility of efficient use of wooden wastes.

We focused on manufacturing nitrogen-doped carbon-based catalysts as potential Pt-free catalysts for polymer electrolyte fuel cells. In order to optimize the electrochemical performance of fuel cells, the relationships between the carbonization treatments performed on pristine and N-doped Sugi wood powders and their electro-catalytic activity is under investigation here.

Experimental

The effect of sintering is studied during carbonization of Sugi (*Cryptomeria japonica*) wood applying a pulsed current sintering technique, in which current is directed straight through graphite dies and the sample, so that the sample is heated from both the inside and outside at the same time. The relationship between the carbonization treatments performed both on pristine and N-doped Sugi wood powder and their electro-catalytic activity was studied in order to optimize the electrochemical performance of fuel cells. Raw materials prepared by mixing carbonized wood powder and melamine were heated under a nitrogen flow in a pulsed current sintering apparatus at 20^{o}C/min in a 700 - 900^{o}C temperature range for 15 min. Physical and chemical investigations (chemical analysis, SEM, TEM, XPS, N_2 adsorption) make it possible to correlate the effects of N-doping and the carbonization parameters with the oxygen reduction reaction (ORR) activity of the carbonized materials.

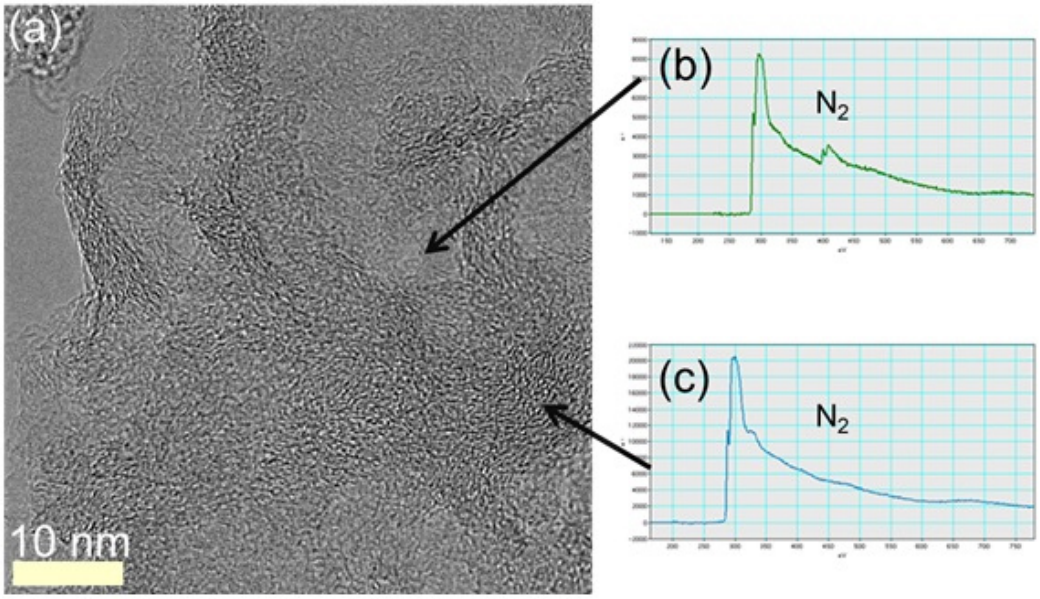

Fig. 1 TEM bright field image and EELS spectra. (a) TEM image of sample (one-step treatment, heat treatment temperature: 600 ^{o}C, heating rate: 20^{o}C/min, time of pre-carbonization: 1hr, time of HTT: 15min, initial concentration of melamine: 75 wt%), (a), (b) EELS spectra, (a) N_2 peak detected, (b) no N_2 peak detected.

Table 1. Analysis of the chemical bonds with XPS of N-doped carbons prepared under heat treatment.

Pre-carbonization temperature	Heat treatment temperature	Heating rate	N-1s (at.%)				C-1s (at.%)						O-1s (at%)		
(°C)	(°C)	(°C/min)	Pyridine	Pyrole	4'	Oxide	C-N	C=C C-H	C-O C-OH	C=O	COOH	Plasmon	C=O	C-O	H_2O ads
	Binding energy (eV)		398.5	400.5	401.2	402.9	287.1	284.6	285.7	287.5	289	291	531.2	532.6	533.3
Two-step heat treatment															
500	600	20	7.9	3.7	1.5	0.6	21.5	42.0	6.1	3.8	2.9	3.2	1.3	2.9	2.5
One-step heat treatment															
-	600	20	6.5	2.8	0.9	0.5	26.0	31.8	12.3	8.1	4.7	5.0	0.7	0.5	0.2
-	700	20	12.7	6.1	3.7	1.3	21.3	24.4	9.8	6.0	2.6	5.2	0.6	1.0	5.5
-	800	20	4.9	5.0	2.0	1.5	23.4	35.9	10.9	5.6	2.7	7.1	0.5	0.1	0.5
-	900	20	1.8	2.3	1.9	1.0	16.8	43.6	12.2	5.7	2.7	7.9	2.1	0.6	1.3

Note. Time of precarbonization: 1hr, Time of HTT: 15min, Initial concentration of melamine: 75 wt%

Table 2. BET surface, pore volume and potential where -10 μA of current density was observed for N-doped carbons of samples prepared under different heat treatment.

Pre-carbonization temperature	Heat treatment temperature	Heating rate	S_{BET} (m^2/g)			V (cm^3/g)			E_{ORR} (V vs. RHE)
(°C)	(°C)	(°C/min)	Total	Micro	Meso	Total	Micro	Meso	
Two-step heat treatment									
500	600	20	132.0	122.4	0.9	0.06	0.05	0.01	0.72
One-step heat treatment									
-	600	20	469.0	339.0	148.0	0.48	0.14	0.37	0.72
-	700	20	283.0	143.0	136.0	0.36	0.06	0.30	0.81
-	800	20	38.0	34.7	5.7	0.06	0.02	0.06	0.72
-	900	20	199.0	194.0	9.4	0.08	0.08	0.01	0.70

Note. Time of precarbonization: 1hr, Time of HTT: 15min, Initial concentration of melamine: 75 wt%, S_{BET}: BET surface area, V: Pore volume, E_{ORR}: Potential where -10μAcm^{-2} of current density was observed.

Results and Discussion

Fig.1 shows a FEG-TEM bright field image and two EELS spectra. Micro graphitic layers were developed in the sample with one- step heat treatment (heat treatment temperature: 600°C, heating rate: 20°C/min, time of pre-carbonization: 1hr, time of HTT: 15min, initial concentration of melamine: 75wt%). More nitrogen was detected in less graphitized areas as shown by the two EELS spectra. Table 1 shows the results of the XPS-analysis for the chemical bonds and Table 2 the BET-results for the surface, pore volume and potential. Nitrogen reacts with the edge of carbons and the atomic concentration of each chemical bond is different depending on the synthesis conditions. Further investigation with gas adsorption measurements and TEM imaging of the nanotexture of these materials is necessary in order to get a better electrochemical performance.

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References

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