Various Carbon Chain Containing Linkages Grafted Graphene with Silver Nanoparticles Electrocatalysts for Oxygen Reduction Reaction

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In this study, we have synthesized an efficient catalyst by various carbon chain containing linkers grafted graphene with silver nanoparticles (AgNPs)-decorated GO-S-(CH2)n-SH (where n = 2, 3, 4 and denoted as GO-Cn-Ag) for oxygen reduction reaction (ORR). The structural and morphological properties have investigated via several instrumental methods. Among those catalysts, the GO-C4-Ag has showed an excellent electrocatalytic performance by cyclic voltammetry (CV) and hydrodynamic techniques for ORR in alkaline media. Hydrodynamic voltammetry reveals that the GO-C4-Ag modified electrode has catalyzed effectively at higher potential. The overall electrocatalytic results showed that the GO-C2-Ag has better activity toward ORR and demonstrated nearly four electron transfer pathway into H2O due to much grafting of linker molecule and smaller size of AgNPs. The value of transferred electron number (n) and other kinetic parameters have demonstrated that the GO-C2-Ag is highly facilitated than that of GO-Ag and other GO-Cn-Ag to electrocatalytic oxygen reduction.

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Graphene, which is discovered by Geim’s group in UK in 2004, is composed of a single sheet of conjugated sp² carbon atoms packed into a honeycomb crystal structure. It is an attractive material due to its unique physical and chemical properties such as its outstanding thickness, tensile strength (130 Gpa), thermal conductivity (5,300 W/mK), allowable current density (108 A/cm²), and mobility (200,000 cm²/Vs). However, the oxidized graphene (GO) surface is highly functionalized with oxygenated groups, such as ketones, epoxides, hydroxyls and carboxylates, which make them targets for covalent modification. Graphene has been recognized and used as an important material in various technologies in chemistry such as, displays, rechargeable batteries, solar cells, automobiles, fuel cells (FCs). In recent years, due to global warming, energy issues are in the spotlight. Thus, many studies have been conducted on carbon nanomaterials supported metal nanoparticles (NPs) for both anodic and cathodic reactions in FCs including oxygen reduction reaction (ORR).

ORR is important for energy conversion systems in FCs and metal air batteries. It is well-known that a platinum (Pt)-based catalyst in an acidic solution has the highest chemical stability among electrochemically active catalysts. However, Pt-based catalysts are too expensive to make FCs commercially viable. Under acidic conditions, due to the high dissociation energy (494 kJ/mol) of oxygen molecules, electrochemical oxygen reduction requires a high superpotential, and the reaction rate is slow. Moreover, Pt has suffered several problems such as, poor drivability and toxic effects of methanol crossover/carbon monoxide in direct methanol fuel cells (DMFCs).

In the last few years, because of these shortcomings of Pt-based electrocatalysts, studies have been conducted to develop alternative non Pt catalysts. Typical alternative metallic catalysts are included with several metals such as silver (Ag), gold, palladium, cobalt, porphyrin, and manganese have been studied. Among these options, Ag, being relatively inexpensive and abundant, is a promising candidate as a cathode electrode catalyst for FCs. It has been reported that the 20% Ag/C catalyst shifts toward negative potentials by about 50 mV in comparison with the onset potential of the 20% Pt/C catalyst and better tolerance toward methanol. Various effects of the Ag/C electro-catalyst on its ORR with the particle size, amount of loading, and bonding with a non-metal were recently studied. To the best of our knowledge, however, there is no reported relationship yet between the linker length and the catalytic activities of Ag-decorated graphene.

Based on the above discussions, the various length linkages between graphene and AgNPs have synthesized and were investigated for ORR in 0.1M NaOH solution. The GO-Cn-Ag catalysts were examined using cyclic voltammetry (CV) and hydrodynamic techniques including rotating ring disk electrode (RRDE) and rotating disk electrode (RDE) techniques. The catalysts showed better ORR activity in the shorter-chain GO-C2-Ag-modified glassy carbon electrodes (GCEs) than that of GO-Ag and other GO-Cn-Ag. The electrocatalyst and the stability toward the ORR were also analyzed through Koutecky-Levich plots, which confirmed that the O2 reduction was proceeded on via a four-electron transfer pathway.

Experimental

Chemicals and reagents.—The graphite powder (~325 mesh, 99.999%), tetrahydrofuran (THF), ethanol, 1,2-ethanediol [HS-(CH2)2-HS; C2], 1,3-propanediol [HS-(CH2)3-HS; C3], and 1,4-butanediol [HS-(CH2)4-HS; C4] were obtained from Sigma-Aldrich. KMnO4, H2SO4, and H3PO4 were purchased from Dae-jeung Co., Korea. AgNO3 was purchased from Inuiho Precious Metals Co., Ltd. NaOH was purchased from Dukasen Pure Chemical Industries Co., Ltd. The membrane filters (pore size: 0.2 μm and diameter: 47 mm; and pore size: 1.0 μm and diameter: 47 mm) were purchased from Milipore Corporation in Bedford and Whatman.

Different length linkages on graphene (GO-Cn-SH).—GO was obtained by oxidizing graphite using the improved Hummers method. Briefly, the GO and the linker materials, HS-(CH2)x-SH (x = 2, 3, and 4), were separately dispersed with tetrahydrofuran (THF) into four round-bottom flasks and stirred at 55 °C for 20 hours before 30-min ultrasonic agitation. The resulting black materials were separated from the mixture by filtration, washed several times with THF, methanol, ethanol, and distilled water (DW), and dried in a vacuum oven at 50 °C for 18 hours.

Synthesis of GO-Cn-Ag.—To verify the support effect, the GO-C2-Ag mixture was prepared by adding 30 mg of GO-C2-SH to 15 mL of DW for 30-minute ultrasonic agitation. Then 0.1M AgNO3 (5 mL) and 0.1M NaOH (2 mL) were added to the mixture and stirred for 20 hours. The GO-C2-Ag products were obtained via centrifugation, washed with DW, and vacuum-dried for 24 hours at 50 °C.

The GO has large surface area and provided with epoxy and hydroxyl functional groups, providing a number of chemically active sites for addition of SH-C2-SH via a condensation reaction.
Scheme 1. Schematic procedures for the preparation of the metal catalysts on the thiolated GO (GO-Cx-Ag).

reaction and subsequently addition of AgNPs onto the linker’s molecules (Scheme 1). As a result, the GO-Cx-Ag has been synthesized with dendrite like structure and consisted of a sheet decorated with AgNPs are well separated.

Physical characterization.— X-ray photoelectron spectroscopy (XPS) was performed with a VG Multilab 2000 spectrometer (Thermo VG Scientific, South-end-on-Sea, Essex, UK) in an ultra-high vacuum. The XPS data analysis program of Avantage 4.54 version (Thermo Electron Corp., England) was used. This system uses an unmonochromatized Mg K (1253.6 eV) source and a spherical section analyzer. Survey scan data were collected using a 50eV pass energy. A field emission scanning electron microscope (FE-SEM) image of the modified electrode was obtained with a JSM-7500F field emission scanning electron microanalyzer (JEOL). The high-resolution transmission electron microscopy (HRTEM) images and energy dispersive X-ray spectroscopy (EDS) were carried out with a TECNAI 20 microscope at 200 kV.

Electrochemical measurement.— For the electrode preparation, a GO-Cx-Ag suspension in water (1 mg/ml) was prepared by introducing a predetermined amount of the corresponding sample under sonication. Then 16 \( \mu l \) of the prepared catalyst ink was dropped onto the surface of a glassy carbon electrode (GCE, 0.5 cm in diameter) prepolished with a 0.05 \( \mu m \) alumina suspension on a polishing cloth (BAS, USA). After the coating, electroreduction was performed between the sweeping potentials of 0 V to \(-1.5\) V at a scan rate of 50 mV/s for 60 cycles in phosphate buffer solution (PBS) at PH 5. Then the GO-Cx-Ag coated GCE was employed for ORR in an O2- and/or Ar-saturated 0.1 M NaOH solution. All the voltammetric measurements were taken using a three-electrode potentiostat [CHI 700C electrochemical workstation (USA)] in a grounded Faraday cage at room temperature. Pt wire was used as an auxiliary electrode. A calibrated Ag/AgCl electrode from Bioanalytical System Inc. (BAS) in a 3M NaCl solution was used as a reference electrode.

Figure 1 shows the base CVs of the GO-Cx-Ag recorded in an Ar-saturated 0.1 M NaOH solution at a scan rate of 50 mV s\(^{-1}\). In the potential range of 0.1 –0.4 V vs. (Ag/AgCl), three peaks were observed: a, b, and c, which were located at about 0.15, 0.21, and 0.26 V, respectively. Moreover, the d peak was located at approximately 0.03 V. The weak peak (a) was due to the dissolution of Ag and formation of a surface monolayer of Ag2O film onto AgNPs. The strongly appeared peaks (b) and (c) were assigned to the formation of the bulk phases of AgOH and Ag2O, and the cathodic peaks were assigned to the reduction of Ag2O back to metallic silver.30

It is known that the electrochemical surface area (ECSA) could reveal the degree of metal utilization in the electrode material. Therefore, these results imply a better utilization of the Ag on the surface of the GO-Cx-Ag with the assistance of smaller size of AgNPs. The ECSA for all catalysts were calculated using Coulombic charge for the reduction of AgO, which is located at around 0 V potential regions in Figure 1 and enlisted in the Table I.

We expected the Ag/C catalyst to be stable for ORR, as reported by Lee et al.31 However, the AgNPs dissolution in 0.1M NaOH in the first measurement yielded the peak (d) current density of about 3.73 mA cm\(^{-2}\), and in the second and third measurements, 3.03 mA cm\(^{-2}\) and 2.11 mA cm\(^{-2}\), respectively.

Ag has a problem of strong dissolution in an open circuit, as seen in the following equation:32

\[
4\text{Ag} + \text{O}_2 + \text{H}_2\text{O} \rightarrow 4\text{Ag}^+ + 4\text{OH}^-.
\]

To solve this problem, a study was conducted on the alkaline electrolyte, 0.1 M NaOH electrolyte for the Ag based catalyst and it showed that the stability of the AgNPs significantly improved.32,33 Therefore, we have used 0.1 M NaOH electrolyte system for avoiding AgNPs dissolution during synthesis and ORR.

Figure 1. The CVs of the GO-Cx-Ag catalysts in an Ar-saturated 0.1 M NaOH solution at 25 °C at a scan rate of 50 mV s\(^{-1}\).
Table I. The physical, electrochemical and kinetic comparisons between all catalysts have given as below.

| Name       | GO-C₂₋Ag | GO-C₃₋Ag | GO-C₄₋Ag | GO-Ag |
|------------|-----------|-----------|-----------|-------|
| Ag wt% (from XPS) | 24.0      | 24.1      | 24.2      | 25.1  |
| Ag loading (μg cm⁻²) | 54.6      | 54.6      | 54.8      | 56.8  |
| ECSA (m² g⁻¹) | 72        | 63        | 53        | 45    |
| $j_0 @ -0.2 \text{ V (mA cm}^{-2}\text{)}$ | 0.598     | 0.312     | 0.270     | -     |
| Tafel slope (mV dec⁻¹.) | 120.2     | 126.5     | 131.5     | -     |
| Onset from LSV (V) | -0.1      | -0.13     | -0.14     | -0.25 |
| Koutecky-Levich plot | $n$ value | 3.88      | 3.75      | 3.59  |
| slope      | 2.26      |           |           | 1.42  |

Results and Discussion

Surface morphology.— The surface morphology of GO-Cₓ₋Ag was characterized with SEM and TEM investigations. The Figure 2 shows the TEM images of GO-Cₓ₋Ag and SEM images of GO-Cₓ₋Ag at Figure 2 insets, respectively. The layer-by-layer assembled 2D sheet-like morphology was observed at GO-Cₓ₋Ag (Figure 2). According to the TEM images, at the shorter chain, GO-C₂₋Ag, high content of AgNPs were appeared onto the surface and the AgNPs size was smaller than that of GO-C₃₋Ag and GO-C₄₋Ag (Figure 2a).

Figure 2. The TEM and SEM (inset) images of the prepared GO-C₂₋Ag (a), GO-C₃₋Ag (b) GO-C₄₋Ag (c) and (d) GO-Ag; the size distribution are displayed in a’, b’ and c’, respectively; the EDS also displayed (e).
Moreover, the AgNPs were uniformly dispersed onto the graphene sheet. The Figure 2b and 2c had also spherical shaped AgNPs and were not uniformly dispersed. Slight agglomeration of NPs was observed which yielded a bigger size distribution. The measurement of spacing lattice planes are 0.22 nm, 0.231 nm, and 0.28 nm, for GO-C2-Ag, GO-C3-Ag and GO-C4-Ag, respectively, which corresponds to the (200) lattice plane of face-centered-cubic structure.35,36

XPS characterization.— The Figure 3a shows the XPS survey spectra for GO-Cx-Ag. All spectra showed the C1s (284 eV), O1s (532 eV), Ag3d (367 eV), and S2p (162 eV) signals. The C/Ag wt% ratio was decreased as 2.55, 2.52 and 2.50 for GO-C2-Ag, GO-C3-Ag, and GO-C4-Ag, respectively. Indicating carbon content is decreasing due to the higher degree of chain grafting in the order of C2 > C3 > C4 onto the graphene. Figure 3b shows the high-resolution S2p spectra. As can be observed in the S2p spectra, at 162.8 eV is corresponded to the double carbon liked S (–C–S–C–) and between 164 eV to 168 eV has no ant identical peaks for SOx.37 This result actually suggests that the constant Ag content is due to higher dispersion with smaller size and vice versa, as observed in TEM analysis.
whereas the ORR onset potential at the GO-C2-Ag was significantly shifted positively to −0.11 V with the limiting diffusion current at −1.2 V being stronger than that of these electrodes. Therefore, the enhanced ORR on GO-C2-Ag due to well dispersion of AgNPs with smaller size and the higher ECSA while the Ag mass loading (16 μl) was same for all GO-Cx-Ag.

**Kinetic studies.**—To analyze the experimental results in this study, we used the simplified model, Scheme 2.\(^{25,40}\) Path 1 shows how O\(_2\) is reduced directly to H\(_2\)O through a four-electron transfer. Path 2 is the sequential reaction path wherein O\(_2\) is first reduced to H\(_2\)O\(_2\) through a two-electron transfer, followed by a two-electron reduction to H\(_2\)O (Path 3), or by the release of the formed H\(_2\)O\(_2\) into the bulk solution (Path 4).

The Figure 5 shows the ORR on GO-Cx-Ag performed by an RDE in the O\(_2\)-saturated 0.1 M NaOH aqueous solution at a scan rate of 10 mV s\(^{-1}\) with various rotating speeds of 100–3600 rpm. For the all GO-Cx-Ag, the limiting diffusion current density increased with an increasing rotation rate, and the ORR onset potentials are −0.1 V, −0.13 V, and −0.14 V, for GO-Cx-Ag (Figure 5a) GO-C2-Ag (Figure 5b) GO-Cx-Ag (Figure 5c) and GO-Ag (Figure 5d) respectively. The potentiometric measurement showed that a shorter chain, GO-Cx-Ag, catalyze at most positive onset potential with higher current density toward ORR. Very significantly, in the limiting current portion (−0.5 V to −1.2 V) of LSV for all GO-Cx-Ag toward ORR has only one step which is favorable for ORR at the electrodes while the two step can be seen in the at GO-Ag electrode only.\(^{25,38}\)

The Figure 5 shows the corresponding Koutecky-Levich plots for GO-Cx-Ag and GO-Ag. In order to determine the kinetic efficiencies of all GO-Cx-Ag, the Koutecky–Levich plots (Figure 5a,b,c, and d, respectively) were constructed from the rotating disk voltammogram data. The Koutecky–Levich plots at different electrode potentials displayed good linearity, and the slopes remained approximately constant at potentials that ranged from −0.3 V to −1.2 V, which suggest that the electron transfer numbers are similar for oxygen reduction at different electrode potentials and represents first order kinetics with respect to O\(_2\).\(^{41,42}\) Moreover, the each Koutecky–Levich plot has a distinct slope which may be indicating the oxygen reduction does not follow the diffusion limited reaction.\(^{41}\)

The number of transferred electron (n) per O\(_2\) molecule was calculated from the slope of Koutecky-Levich plot which derived from Koutecky-Levich equation:\(^{42,43}\)

\[
 J^{-1} = J_k^{-1} + J_L^{-1} = J_k^{-1} + \left( B \omega^{1/2} \right)^{-1} \tag{1}
\]

\[
 J_k = \frac{1}{n F K C_o} \tag{2}
\]

\[
 B = 0.62 n F C_o (D_o)^{2/3} v^{-1/6} \tag{3}
\]

Where in j is the measured current density, \( J_k \) is the kinetic current density, \( J_L \) is the limiting diffusion current density, \( \omega \) is the rotation rate of the electrode, \( n \) is the transferred electron number per oxygen molecule in ORR, \( F \) is the Faraday constant (\( F = 96,485 \) C mol\(^{-1}\)), \( C_o \) is the concentration of O\(_2\) (\( C_o = 1.2 \times 10^{-6} \) mol cm\(^{-3}\)), \( D_o \) is the diffusion coefficient of O\(_2\) in the bulk solution.

**Figure 4.** The CV curves of oxygen reduction on the GO-Cx-Ag and GO-Ag electrodes at a scan rate of 50 mV s\(^{-1}\) (a), and RRDE curves for ORR on the GO-Cx-Ag electrodes in same solution at a scan rate of 10 mV s\(^{-1}\) and the ring electrode was constant on 1.2 V (b).
Figure 5. RDE measurements for the ORR on GO-Cₓ-Ag modified electrodes at 100–3600 rpm at a scan rate of 10 mV s⁻¹ in an O₂-saturated 0.1M NaOH solution, the corresponding Koutecky-Levich plots for GO-Cₓ-Ag at different electrode potentials.

is the diffusion coefficient of O₂ in the 0.1M NaOH solution ($D_o = 1.9 \times 10^{-5}$ cm² s⁻¹), and $\nu$ is the kinetic viscosity of the electrolyte ($\nu = 0.01$ cm² s⁻¹).

Figure 6a, in which the $n$ values were found to be dependent on the potential for electrodes. In particular, the $n$ value increased with a decrease in the negative potential. The $n$ value for ORR at the GO-C₂-Ag electrode is always higher than that of GO-Cₓ-Ag and GO-Cₓ-Ag electrodes over the potential range from −0.6 to −1.2 V. Within the range the $n$ value from 3.8 to 4 which suggests the ORR proceeds is definitely via a four-electron pathway on GO-C₂-Ag. Although, the $n$ values of GO-Cₓ-Ag and GO-Cₓ-Ag are more than 3.5 and that also suggest nearly four-electron pathway. Therefore, the number of
Figure 6. The kinetic comparison for the ORR catalyzed by GO-C_x-Ag (a) Transferred electron number (b) the corresponding H_2O_2 production and (c) Tafel slope.

electron per O_2 molecule was inversely proportional to the slope as observed.44

According to Fig. 6b, the H_2O_2 proportion at GO-C_x-Ag is much lower than that of GO-Ag. This is also consistent with the relatively high calculated transferred electron number per O_2. Among all GO-C_x-Ag, the ORR at the GO-C_2-Ag electrode has produced significantly low H_2O_2.

To further analyze the kinetic parameter in the ORR, the Tafel investigation was done for GO-C_x-Ag electrodes modified (Figure 6c). Generally, there are two Tafel slopes have been observed in previous studies i.e. 120 mV/dec. and 60 mV/dec.45,46 The 60 mV/dec. indicates the rate-limiting step for the ORR and the 120 mV/dec. indicates the rate-determining processing to the transport of oxygen to the electrocatalyst.47

The Tafel slopes obtained at kinetic regions (between −0.3 and −0.2) were 120.2, 126.5, and 131.6 mV dec⁻¹, for GO-C_2-Ag, GO-C_3-Ag and GO-C_4-Ag, respectively. The small Tafel slope is generally indicating faster electron transfer kinetics and less poisoning to the metal surface.5,48 However, the results indicate that the similar behaviors of the Tafel slopes and the reaction mechanism and the rate-determining step are the same in GO-C_x-Ag and much better at GO-C_2-Ag among all catalysts.2,41

Conclusions

In this study, the effect of the length of the linker molecules was investigated by AgNPs-supported graphene on electrocatalytic activity toward ORR. The microscopic image of GO-C_2-Ag consisted of sheets decorated with many AgNPs with smaller particle size than GO-C_3-Ag and GO-C_4-Ag. Moreover, XPS suggests a much amount of smaller linker molecules can be grafted via a condensation reaction onto graphene sheet. To determine the catalytic activity, the CV and RDE techniques were used for the ORR in 0.1 M NaOH solution. All the electrochemical and the kinetic results were indicating that a better catalysis was done upon shorter chain linked catalyst, GO-C_2-Ag, than that of GO-Ag and other higher chain linked catalysts, GO-C_3-Ag and GO-C_4-Ag. Therefore, the GO-C_2-Ag catalyst had superior catalytic activity toward ORR through four-electron transfer pathway.

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