

Tribochemistry of Diamond-like Carbon: Interplay between Hydrogen Content in the Film and Oxidative Gas in the Environment

Seokhoon Jang, Muztoba Rabbani, Andrew L. Ogrinc, Maxwell T. Wetherington, Ashlie Martini, and Seong H. Kim*



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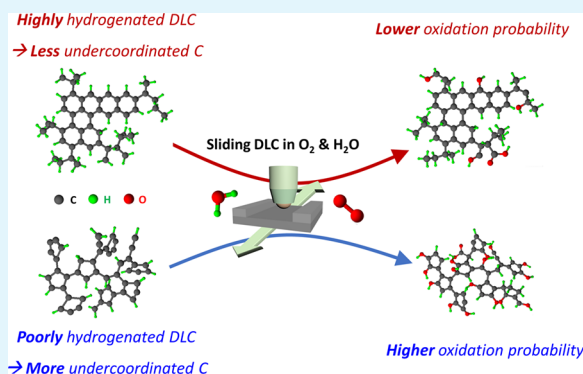
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ABSTRACT: The lubricity of hydrogenated diamond-like carbon (HDLC) films is highly sensitive to the hydrogen (H) content in the film and the oxidizing gas in the environment. The tribochemical knowledge of HDLC films with two different H-contents (mildly hydrogenated vs highly hydrogenated) was deduced from the analysis of the transfer layers formed on the counter-surface during friction tests in O₂ and H₂O using Raman spectroscopic imaging and X-ray photoelectron spectroscopy (XPS). The results showed that, regardless of H-content in the film, shear-induced graphitization and oxidation take place readily. By analyzing the O₂ and H₂O partial pressure dependence of friction of HDLC with a Langmuir-type reaction kinetics model, the oxidation probability of the HDLC surface exposed by friction as well as the removal probability of the oxidized species by friction were determined. The HDLC film with more H-content exhibited a lower oxidation probability than the film with less H-content. The atomistic origin of this H-content dependence was investigated using reactive molecular dynamics simulations, which showed that the fraction of undercoordinated carbon species decreased as the H-content in the film increased, corroborating the lower oxidation probability of the highly-hydrogenated film. The H-content in the HDLC film influenced the probabilities of oxidation and material removal, both of which vary with the environmental condition.

KEYWORDS: hydrogenated diamond-like carbon, superlubricity, surface oxidation, environmental sensitivity, shear-induced graphitization



1. INTRODUCTION

Diamond-like carbon (DLC) has superior mechanical properties¹ and wear protection,² which makes it attractive for solid lubrication in engineering systems such as extreme ultraviolet lithography instruments,^{3,4} mechanical shaft seals,^{5,6} bearings,⁷ etc. The C–C connectivity in DLC changes with its chemical composition,^{8,9} which is, in turn, very sensitive to deposition temperature¹⁰ and precursor gases used during synthesis.^{1,11–13} For example, when DLC is produced via a plasma-enhanced chemical vapor deposition (PECVD) using a precursor gas of C₂H₂, the DLC contains ~30 at.% of hydrogen (H); this “mildly hydrogenated” DLC was previously called NFC-10,¹¹ but will be called 30-HDLC in this study.¹⁴ When DLC is produced via the same PECVD process with a mixture of 25% CH₄ and 75% H₂, the DLC contains ~40 at.% of H; this “highly hydrogenated” DLC was previously called NFC-6,¹¹ but will be called 40-HDLC here.¹⁴ The 40-HDLC has a larger graphitic sp²-C domain size than the 30-HDLC.¹⁴

The friction behavior of these HDLC coatings varies drastically depending on the environmental condition in which friction is tested.^{1,12–15} In vacuum^{16,17} or dry N₂,^{18–20} the coefficient of friction (COF, μ) of 40-HDLC usually starts high (~0.25) and, after a transient or run-in period, decreases

to a superlubricous value ($\mu \leq 0.01$). On the contrary, 30-HDLC has a higher COF (>0.7) after the run-in period in the same vacuum or inert conditions.^{2,12,14,21,22} In ambient air conditions, however, the COFs of both 30- and 40-HDLC converge to around 0.1–0.2.^{17,23,24} This environment dependence has been attributed to defect sites at the HDLC surface exposed by sliding, which react with molecules impinging from the gas environment.^{17,19,20,23–26}

Although the environmental sensitivity of HDLC surfaces with different H-contents and sp²-graphitic domains has been well documented, its molecular origins are not well understood. This lack of understanding is associated with the unstable nature of defect sites exposed by friction. The wear tracks formed on HDLC in an inert atmosphere such as dry N₂ are readily oxidized even with a brief exposure to ambient air;^{27–30} this makes it extremely difficult to move the sample,

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without altering its surface chemistry, from the environment-controlled tribo-testing system to X-ray photoelectron spectroscopy (XPS) or X-ray absorption spectroscopy (XAS) systems. Thus, ex situ chemical analyses of wear tracks formed in an inert atmosphere are affected by the contribution from the air-oxidized surface layer formed while moving the sample. Similarly, HDLC surfaces tested in a controlled environment can be oxidized further upon exposure to air. The thickness of the air-oxidized layer is self-limiting to 1–2 nm due to the transport limit of oxidants in air (O_2 and H_2O) into the amorphous carbon network at room temperature.^{27–29,31} This is much thinner than the probe depth of XPS and XAS,^{15,24} but it still affects the analysis.

To investigate the origin of superlubricity of HDLC without complications due to air-oxidation, in situ transmission electron microscopy (TEM)^{32,33} and in situ Raman spectroscopy^{18,34,35} have been employed and these approaches indeed were able to find shear-induced evolution of the DLC into more sp^2 -graphitic structures. However, they still cannot provide critical insights relevant to the environmental sensitivity of HDLC films. TEM needs to be operated in high vacuum conditions and probes only small regions at a limited number of locations;³⁶ thus, it is often difficult to evaluate statistical significance across the entire sliding contact region of amorphous carbon materials which are inherently inhomogeneous.^{14,37} In the case of in situ Raman analysis, the probe depth is so deep (for example, >500 nm if the excitation laser wavelength is 532 nm) that its analysis of the wear track is affected by the contribution of the bulk HDLC film.¹⁴

One possible way of avoiding such complications is ex situ analysis of the transfer layer that remains on the counter-surface after tribo-testing of HDLC in controlled environments. Since the tribological interface is not in equilibrium, its chemistry and structure will inherently have a path or history dependence. Thus, the *post-mortem* analysis of the transfer layer could provide critical insights into the chemistry and structure of the shear plane *during* the friction test, which cannot be obtained (or are difficult to obtain) otherwise. Transfer layers formed on counter-surfaces have been found to be 100–200 nm-thick;^{14,18} thus, they can be analyzed with Raman spectroscopy if the counter-surface does not have any Raman signals in the spectral region of the transfer layers. Indeed, this approach of employing ex situ Raman analysis of the transfer layer was able to identify differences in the H-content and degree of shear-induced graphitization that could be related to the friction behavior of 30- and 40-HDLC in inert (N_2) and reducing (H_2) conditions.¹⁴

In this study, we used the same ex situ Raman analysis approach in an attempt to understand the sensitivity of friction of 30- and 40-HDLC to the presence of O_2 and H_2O in the tribo-testing environment. We also evaluated if the ex situ XPS analysis of the transfer layer could provide additional insights into the chemical composition of the transfer layer oxidized during the friction test in O_2 and H_2O environments. These ex situ analyses of transfer layers were then complemented by analysis of the O_2 and H_2O partial pressure dependence of HDLC friction with a Langmuir-type reaction kinetics model, corroborated by reactive molecular dynamics (MD) simulations. Combining all these results, a more comprehensive model was proposed to describe the dynamic and reactive processes occurring at the tribological interface of HDLC under the impingement of oxidizing agents in ambient air (O_2 and H_2O).

2. EXPERIMENTAL DETAILS

2.1. Preparation of HDLC Films. Both 40-HDLC and 30-HDLC substrates were produced on Si(100) wafers via the PECVD process, which was described fully elsewhere.^{11,13} In short, after the Si substrate was sputtered in an argon plasma, a bonding layer of ~ 100 nm-thick silicon was deposited. The substrate was exposed to a reactive plasma produced from a mixture of 25% CH_4 and 75% H_2 to create ~ 1 μm -thick 40-HDLC. Similarly, 30-HDLC was fabricated using the same procedure with plasma of 100% C_2H_2 and had similar thickness. The endogenous hydrogen content of the 40- and 30-HDLC films (40 and 30 at.%) was determined by the hydrogen forward scattering (HFS) method, as reported previously.³⁸

2.2. Bidirectional Ball-on-Flat Tribo-Testing. The COF was measured with a custom-built ball-on-flat bidirectional-reciprocating tribometer.^{39–41} All friction tests were repeated at least three times to confirm reproducibility (Figures S4 and S5). Before the friction tests, the HDLC surfaces were rinsed with ethanol, and then with deionized water, followed by blow-drying with nitrogen gas to remove any contaminants.⁴² The HDLC sample was mounted in a continuous gas flow cell, and an AISI 440C bearing-grade stainless-steel (SS) ball with a diameter of 3 mm and a root-mean-square (RMS) surface roughness of ~ 10 nm was placed on top of the HDLC substrate as the counter body with an applied load of 2 N.⁴³ The reciprocating motion was conducted at a sliding speed of 3 mm/s over a span of 2.5 mm. At this sliding speed and normal load, the temperature rise produced by frictional sliding at the HDLC surfaces was estimated to be only ~ 3 K,²⁵ which implies that the effect of frictional heat on the sliding interface is negligible in this study.

The extended Hertzian contact mechanics theory,⁴⁴ that accounts for the effects of both the Si substrate and HDLC coating, was used to estimate contact area and maximum contact pressure. On the 40-HDLC film which had an elastic modulus of 55 GPa,^{1,43} the contact area (A_{Hertz}) and the maximum contact pressure ($P_{Contact}$) were estimated to be $2920 \mu m^2$ and 1.06 GPa, respectively. The 30-HDLC had an elastic modulus of 200 GPa;¹ the same theory estimated the contact area $A_{Hertz} = 2750 \mu m^2$ and the maximum contact pressure $P_{Contact} = 1.08$ GPa. The hardness of 40- and 30-HDLC was reported to be 8 and 27 GPa, respectively.^{1,43}

An ultrahigh purity N_2 gas (purity >99.994%; based on the supplier's specification) was flown continuously into the environmental cell during the friction test as a background gas carrying oxidizing gases. The dry oxygen gas environment was prepared by mixing the nitrogen gas stream with an ultrahigh purity oxygen gas (UHP-grade, purity >99.994%; based on the supplier's specification) at a pre-determined ratio for a desired partial pressure of oxygen. The relative humidity (RH) was controlled by mixing the same nitrogen gas with a saturated stream of water vapor at a pre-determined ratio.⁴⁵ All experiments were carried out at ambient pressure and room temperature.

2.3. Raman Analyses of Pristine HDLC and Transfer Layers on SS. Raman analysis of pristine HDLC and transfer layers was performed using a Horiba LabRam system with a 100 $\times$ objective lens ($NA = 0.95$). The Raman spectrometer was calibrated based on the Si line at 520 cm^{-1} . Neutral density filters were utilized to minimize carbon sample burning and the data acquisition time was 5 s with a laser power of 1 mW. At this condition, the estimated power density was $\sim 2.7 \times 10^5 \text{ W/cm}^2$ and no beam damage of HDLC was noticed. A monochromatic 532 nm laser was chosen to empirically estimate the H content, elastic modulus, and density of HDLC and transfer layers.⁴⁶ For the empirical quantification of the sp^3 -C content of pristine HDLC and transfer layers,^{47–50} Raman spectra were measured at multiple wavelengths (229, 364, 488, 532, and 633 nm) (see Figures S2 and S3). A 300 gr/mm grating was used for 532 and 633 nm lasers, and a 600 gr/mm grating was used for 229, 364, and 488 nm lasers.

2.4. XPS Analyses of Pristine HDLC and Transfer Layers on SS. XPS analysis of pristine HDLC and transfer layers was carried out using a PHI VersaProbe III spectrometer to probe the oxidation state, especially the O/C ratio, of these samples. The X-ray source was a monochromatic Al $K\alpha$ source. The transfer layer sample was exposed

to ambient air for at least 10 min during the sample transfer from the environment-controlled tribo-testing system to the XPS chamber. To compensate for sample charging, the peak position of the saturated C 1s peak was adjusted to 285 eV. High-resolution XPS spectra of C 1s and O 1s were obtained at a pass energy of 69 eV. The atomic concentrations of carbon and oxygen were estimated from the peak area measured in the high-resolution spectra after correcting with the relative sensitivity factors determined for our spectrometer using standard samples. The C 1s peaks were fitted with the CASA software into four components, 285.0, 286.4, 287.6, and 289.0 eV, with the same line shape and width. The background was removed by the Shirley method.

2.5. Contact Angles of Water and Diiodomethane (DIM) on 30- and 40-HDLC Films. The measurement of contact angles of water and DIM on 30- and 40-HDLC films was based on the sessile drop method. The contact angles were measured using a ramé-hart Model 295 automated goniometer/tensiometer. After a single drop of liquid on 30- and 40-HDLC films, the contact angle was measured 10 times for 1 s and then averaged. Fowkes theory was utilized to calculate surface energy.⁵¹

2.6. Computational Methods. Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) and OVITO were used for reactive molecular dynamics (MD) simulations and visualizations.^{52,53} The interatomic interactions were modeled using a ReaxFF force field that was capable of reproducing physical properties of various carbon allotropes and previously used to study the wear and tribochemical reactions of carbon materials in H₂ gas.⁵⁴ In MD, an amorphous carbon (a-C) structure was produced by rapidly quenching a high temperature carbon structure in four steps. The first three steps were performed in the microcanonical ensemble (NVT) using the Nosé–Hoover thermostat with a damping parameter of 20 fs. First, initial structures were heated from room temperature to 8000 K at a heating rate of 1000 K/ps. Second, the model was equilibrated at 8000 K for 10 ps. Third, the temperature was decreased to 300 K at a rate of 770 K/ps. Finally, the amorphous structures were relaxed at constant pressure and temperature (NPT) using the Nosé–Hoover thermostat and barostat with damping parameters of 20 and 200 fs, respectively, for 40 ps until the potential energy reached a steady state. The dimensions of a-C after this process were approximately 1.9 × 3.15 × 4.5 nm³. It should be noted that the surface of the model a-C may not be the same as the HDLC surface in the friction tests due to the nonequilibrium nature of this material system. Nonetheless, the general trend of chemical reactivity of a-C surfaces with different H-contents is expected to provide insights relevant to the HDLC experiments.

Four a-C structures were constructed with homogeneous concentrations of hydrogen of 10, 20, 30, and 40 at.%; they will be called a-C:10-H, a-C:20-H, a-C:30-H, and a-C:40-H. The height of the simulations cells was extended to create a-C surfaces such that the model systems were 4.2 × 3.15 × 4.5 nm³, followed by the thermal equilibration in the NVT ensemble again. To model the oxidation of a-C:H with water and oxygen, either 150 water molecules or 286 oxygen molecules were placed above the a-C:H films (see Figure S1). The boundaries of the model systems in the surface-normal direction were defined by fixing the positions of the bottom most 0.3 nm of a-C:H and adding a reflective wall at the top of the model system. Periodic boundary conditions were applied in the directions in the plane of the surface. The reaction of a-C:H with water or oxygen molecules was allowed by running the simulation in the NVT ensemble at room temperature. The formation of C–O bonds between C in a-C:H and O in water or oxygen was tracked during the simulations for 200 ps, after which no new bonds were observed to form.

3. RESULTS AND DISCUSSION

3.1. Chemical Properties of Bulk HDLC and Its Top Surface. The pristine 30- and 40-HDLC films (before friction testing) were analyzed with Raman spectroscopy (probing several hundred nm's) and XPS (probing top ~10 nm). In the

Raman spectra, shown in Figure 1a,b, there are two characteristic bands, a D band at ~1350 cm⁻¹ and a G band

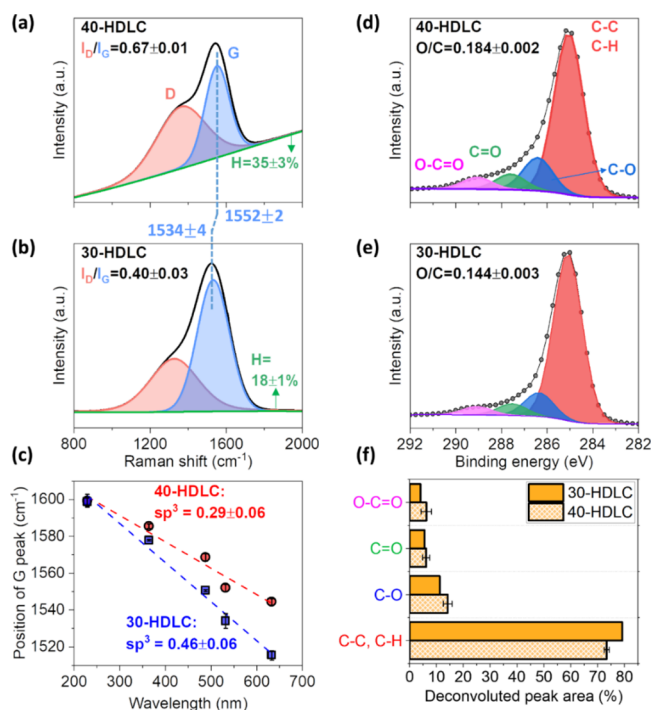


Figure 1. Deconvoluted Raman spectra collected from pristine surfaces of (a) 40-HDLC and (b) 30-HDLC (data collected in our previous study¹⁴). (c) Position of the Raman G band as a function of wavelength of excitation laser for empirical estimation of sp³-C content inside pristine HDLCs. Raman spectra collected with different excitation wavelengths (229, 364, 488, 532, and 633 nm) are shown in Figure S2 in the Supporting Information. Deconvoluted high-resolution C 1s XPS spectra of (d) 40-HDLC and (e) 30-HDLC along with its O/C ratio in the inset and (f) deconvoluted peak area of C-bonds.

at ~1580 cm⁻¹, arising from the breathing modes of sp² graphitic carbon in ring structures and the stretching modes of sp² or sp³ carbons in chain and ring structures, respectively.^{46,55} The intensity ratio of these two bands (I_D/I_G) was related to the size of graphitic sp²-C domain in films.^{46,55} Furthermore, the sp³-C content (Figure 1c) was quantified from the dispersion of the G band position (see Figure S2) using an empirical correlation.^{14,47–50} The H-content of the film was calculated from the fluorescence background in this spectral region, and the density and modulus were approximated from the G-band width using empirical equations.^{14,56–59} All these properties, summarized in Table 1, indicated that 40-HDLC has a larger graphitic domain size, more sp²-C content, and higher H-content than 30-HDLC.

The XPS analysis showed a slightly more oxygen content in the 40-HDLC surface (Figure 1d) than the 30-HDLC surface (Figure 1e). The deconvoluted C 1s XPS signal showed that the fraction of C–O and O–C=O species was higher in the air-oxidized surface of 40-HDLC than that of 30-HDLC (Figure 1f). The thickness of the air-oxidized layer was previously estimated to be 1–2 nm.^{27–29} The polar component of surface energy calculated from contact angle measurements (see Table 1 and Figure S2c) was larger for the 40-HDLC than the 30-HDLC surface, which appeared to correlate with the

Table 1. Structural Properties of Pristine 40- and 30-HDLC Films Determined from Raman Analysis,^{56,57} Chemical Composition from XPS, and Surface Energy from Contact Angle Measurement (See Figure S2c)^a

		40-HDLC	30-HDLC
Raman band parameters	I_D/I_G	0.67 ± 0.01	0.40 ± 0.03
	G_{Pos} [cm^{-1}]	1552 ± 2	1534 ± 4
	G_{FWHM} [cm^{-1}]	153 ± 1	199 ± 4
physical properties calculated by processing Raman spectral features with empirical equations	fraction of sp^3 C (sp^2 -C)	0.29 ± 0.06 ($0.72 \pm 0.06^\dagger$)	0.46 ± 0.06 ($0.51^\ddagger$)
	H content [at. %]	35 ± 3 ($\sim 40^\S$)	18 ± 1 ($\sim 30^\S$)
	elastic modulus [GPa]	200 ± 2 ($\sim 60^\parallel$)	415 ± 20 ($\sim 200^\parallel$)
	density [g/cm^3]	1.94 ± 0.01	2.44 ± 0.05
atomic concentration determined from XPS C 1s and O 1s spectra	C [at. %]	84.5 ± 0.1	87.4 ± 0.2
	O [at. %]	15.5 ± 0.1	12.6 ± 0.2
surface energy [mN/m] obtained from contact angle measurements	dispersive energy	42.7 ± 0.3	42.6 ± 0.2
	polar energy	16.0 ± 0.5	12.2 ± 2.1
	surface energy	58.7 ± 0.3	54.8 ± 2.3

^aThe values denoted by $\dagger$, $\ddagger$, $\S$, and $\parallel$ in the parentheses are from previous studies using NEXAFS,²⁸ electron energy loss spectroscopy (EELS),⁶⁰ hydrogen forward scattering (HFS),³⁸ and nano-indentation,^{1,43} respectively. Note that the physical properties determined from Raman analysis should be interpreted as a qualitative trend only because they were derived from the empirical correlations.

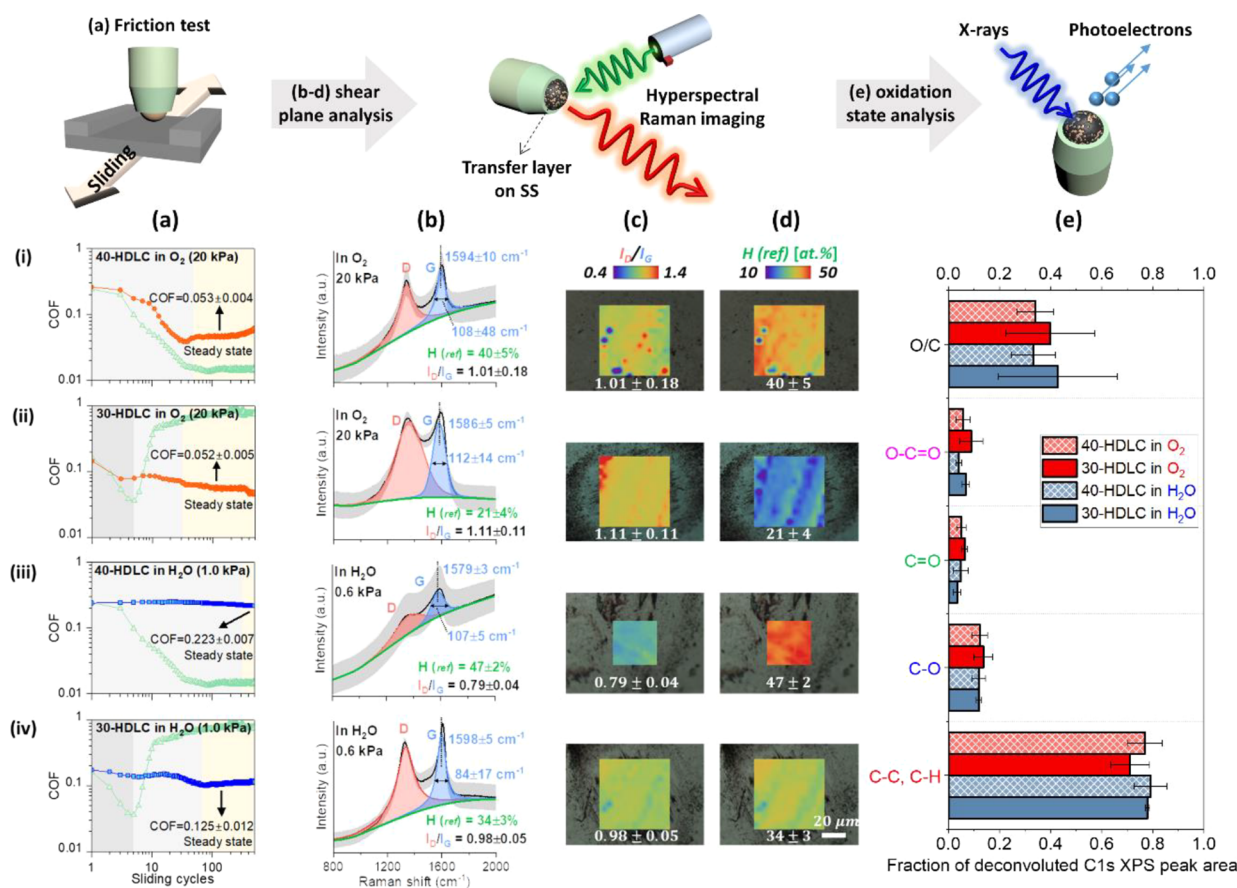


Figure 2. (a) COF measured with SS on (i) 40-HDLC and (ii) 30-HDLC in O₂ (shown with an orange symbol) and (iii) 40-HDLC and (iv) 30-HDLC in H₂O (shown with a blue symbol). The COF of each HDLC measured in dry N₂ is shown with green symbols as a reference in each panel (the COF data in dry N₂ collected in our previous study^{14,25}); the reproducibility of the COF data of 30-HDLC can be checked in Figures S4 and S5; the reproducibility of the COF data of 40-HDLC can be found in the previous publication.²⁵ (b) Raman spectra of the transfer layers formed on SS after sliding in O₂ and H₂O. (c) Raman I_D/I_G maps and (d) Raman H-content maps superimposed on the optical image of the transfer layers. (e) Oxidation state of the transfer layers determined with its high-resolution C 1s and O 1s XPS spectra. All quantitative values in Figure 2a,b are summarized in Table S4 in the Supporting Information. In (b), the gray-shaded regions indicate the standard deviation of the Raman spectrum calculated from the 225-pixel hyperspectral map. Optical images and histograms of the data in (c) and (d) are shown in Figure S6 in the Supporting Information.

higher oxygen content of 40-HDLC than 30-HDLC film (Table 1). Since the dispersive component was similar, the

total surface energy was higher for the air-oxidized 40-HDLC surface than the air-oxidized 30-HDLC surface.

3.2. Analysis of the Transfer Layer Formed in O₂ and H₂O Environments. Figure 2a shows how the COFs of 30- and 40-HDLC films were affected by the environmental condition. Regardless of the test environment, the initial COF of 40-HDLC (0.223 ± 0.007) was higher than that of 30-HDLC (0.125 ± 0.012). Since both films were expected to have a similar contact area (see Section 2.2), the difference in initial COF must originate from something other than the contact size. The most likely cause would be the surface chemistry difference, i.e., a slightly higher O/C ratio of the air-oxidized top surface of 40-HDLC (0.184 ± 0.002) than 30-HDLC (0.144 ± 0.003), which led to a slightly higher surface energy (see Table 1 and Figure S2c). After the run-in period, during which the air-oxidized films were removed by frictional shear⁶¹ and shear-induced graphitization occurred,^{14,18,19,32–34} 40-HDLC exhibited an ultra-low COF ($\mu \approx 0.012 \pm 0.003$) in dry N₂, while 30-HDLC showed a very high COF ($\mu > 0.8$). The 40-HDLC surface lost this superlubricity in the presence of O₂ and H₂O; in contrast, the presence of such gases lowered the steady-state COF of 30-HDLC (Figure 2a).

Ex situ Raman analysis of the transfer layers was conducted to obtain structural information of the shear plane.¹⁴ The Raman spectra averaged over a large area of the transfer layers retrieved after the COF experiments are shown in Figure 2b, and their I_D/I_G and H-content maps are displayed in Figure 2c,d, respectively. In both O₂ and H₂O environments, the degree of hydrogenation was higher for the transfer layers formed from 40-HDLC ($40 \pm 5\%$ after the test in O₂ and $47 \pm 2\%$ after the test in H₂O) than those formed from 30-HDLC ($21 \pm 4\%$ in O₂ and $34 \pm 3\%$ in H₂O). Note that the estimated H-content of these oxidized layers in O₂ and H₂O was based on the Raman empirical correlation of pristine or non-oxidized HDLC films,^{14,56–59} thus, they should be taken as rough estimates, not accurate values.

Although the H-contents in the transfer layers formed from 30- and 40-HDLC in O₂ and H₂O environments appeared quite different from each other (Figure 2b,d), all transfer layers showed a significant degree of shear-induced graphitization. Compared to the pristine film, the I_D/I_G ratio increased substantially, the G-band position was significantly blue-shifted, and the G-band width was much narrower, which collectively indicates the occurrence of shear-induced graphitization. The G-band dispersion also showed that the sp³-C fraction in the transfer layer was quite low (<0.08 ; see Figure S3), confirming a high degree of sp²-C in the transfer layer. It was noted that the degree of graphitization of the transfer layer for 30- and 40-HDLC in O₂ and H₂O environments was quite comparable to that of the super-lubricious transfer layer formed from 40-HDLC in N₂ gas (green data points in panels (i) and (iii) of Figure 2a).¹⁴ This suggested that shear-induced graphitization was not the dominant factor governing friction of HDLC; the surface chemistry of the newly exposed surface (or defect sites) during the friction test must play an important role.⁶²

We evaluated if XPS analysis could detect any meaningful differences in chemical composition of the transfer layer. Figure 2e compares the O/C atomic ratio as well as oxygen speciation of the top ~ 10 nm region of the transfer layers formed in different conditions (two HDLCs and two environmental conditions). The O/C ratios of all transfer layers formed by friction tests in O₂ and H₂O environments (Figure 2e) were higher than those of the air-oxidized surfaces of the pristine films (~ 0.14 for 30-HDLC and ~ 0.18 for 40-

HDLC; Figure 1d,e). However, it could not be determined if this difference really reflects the compositional difference or is simply due to different film structures such as the size of the graphitic domain. If the film structure is different, then the degree of oxidation by air during the sample transfer from the tribo-testing cell to the XPS chamber would also be different. The variance in the O/C ratios among the transfer layers was found to be statistically insignificant ($p > 0.47$ in analysis of variances (ANOVA)).

Combining the Raman and XPS analyses of the transfer layers, it can be concluded that both shear-induced graphitization and oxidation of the sliding interface take place in oxidizing (O₂ and H₂O) environments. Compared to the transfer layers formed from 30- and 40-HDLC in inert (N₂) or reducing (H₂) environments,¹⁴ the degree of graphitization (or graphitic nature) was found to be even larger in the oxidizing environments (Figures 2b and S3). In vacuum, dry N₂, or dry H₂ environments, it has been hypothesized that the degree of shear-induced graphitization of the sliding interface is a main factor governing the COF of HDLC.^{14,18,32–34} However, here, the COF of 40-HDLC was significantly higher in oxidizing environments (Figure 2a) as compared to the inert and reducing environments.¹⁴ The COF of 30-HDLC was also significantly higher in oxidizing environments (Figure 2a) as compared to the reducing H₂ environment,¹⁴ even though the degree of shear-induced graphitization was higher. Thus, the high friction in the oxidizing environment must have been due to the oxidation of the graphitized surface by O₂ and H₂O molecules impinging from the gas phase.

3.3. Kinetics of Environmental Reactions. During the gas exposure between consecutive sliding cycles, the shear-exposed surface was oxidized by reactions with molecules from the gas phase; the reaction products were then removed during sliding. By fitting the steady-state COF measured in various partial pressure of O₂ and H₂O with the Langmuir-type kinetics model, the oxidation rate constant (k_{oxi}) of the surface as well as the removal probability (γ) of reaction products by friction could be extracted.²⁵ This model assumes that the measured COF is the weighted sum of COFs of the unoxidized (μ_{HDLC}) and oxidized surfaces (μ_{oxi}) within the sliding contact region. The COFs of both conditions (μ_{HDLC} and μ_{oxi}) were estimated through control experiments (see Figure S7).²⁵ Once the oxidation rate constant was obtained, the oxidation reaction probability could be estimated by simply dividing the rate constant by the partial pressure since the molecular impingement frequency is proportional to the pressure, i.e., $\alpha = k_{\text{oxi}}/P$. The oxidation reaction probability in O₂ (α^{O_2}) and H₂O ($\alpha^{\text{H}_2\text{O}}$) is discussed in Figure 3. The removal probability (γ^{O_2} and $\gamma^{\text{H}_2\text{O}}$) is discussed in the Section 3.4.

As shown in Figure 3, the oxidation probability of 30- and 40-HDLCs in O₂ and H₂O environments is on the order of $10^{-4} - 10^{-2} \text{ kPa}^{-1}\cdot\text{s}^{-1}$. These values are quite comparable magnitude-wise, to the hydrogenation reaction probability of unsaturated hydrocarbons on highly reactive noble metal catalysts such as Pt and Pd ($\sim 10^{-2} \text{ kPa}^{-1}\cdot\text{s}^{-1}$).^{63,64} In both HDLC cases, $\alpha^{\text{H}_2\text{O}}$ is 3–4 times larger than α^{O_2} . This difference could be ascribed to the higher sticking coefficient of H₂O molecules than O₂.^{65,66} Unlike O₂, H₂O can have hydrogen bonding interactions among physisorbed molecules and thus a longer residence time at the surface.

In Figure 3, it is also noted that the oxidation reaction probability of 30-HDLC by O₂ and H₂O is significantly larger

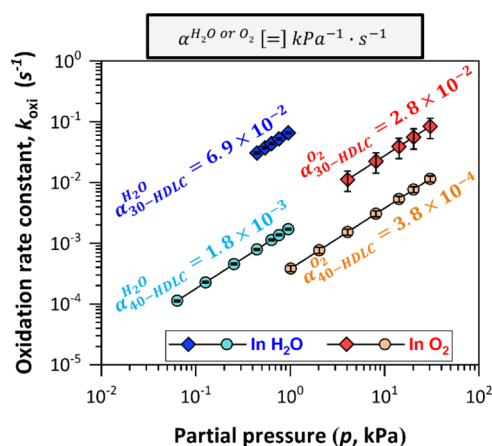


Figure 3. Oxidation rate constant of 30-HDLC and 40-HDLC as a function of partial pressure of H₂O and O₂ ($P_{\text{H}_2\text{O}}$ and P_{O_2}) calculated by fitting the COF vs sliding cycle plot in various $P_{\text{H}_2\text{O}}$ and P_{O_2} with the Langmuir-type kinetics model.²⁵ The fit results of 30-HDLC can be found in Figure S5 in the Supporting Information (see our previous study²⁵ for the fit results of 40-HDLC in the same gas conditions). To fit the sliding-cycle dependence of COF, the COFs of the fully oxidized (μ_{oxi}) and unoxidized surface (μ_{HDLC}) of 30-HDLC were determined from the control experiment described in Figure S7 in the Supporting Information (see our previous studies for μ_{oxi} and μ_{HDLC} of 40-HDLC).^{15,25,61}

than that of 40-HDLC. The origin of this difference was investigated using reactive MD simulations of a-C with four different H-contents interacting with O₂ or H₂O. The carbon atoms in the a-C that chemically reacted with O or H were tracked and used for kinetics analysis. Figure 4a,d plots the fraction of yet-to-be-reacted carbon atoms (θ ; $0 \leq \theta \leq 1$) as a function of time for simulations with O₂ and H₂O, respectively. The fitting of this temporal change ($\frac{d\theta}{dt}$) required a linear combination of two exponential decay functions:

$$\frac{d\theta}{dt} = \theta_1 \cdot \exp(-k_1 \cdot t) + (1 - \theta_1) \cdot \exp(-k_2 \cdot t) \quad (1)$$

where θ_1 is the fraction of reactive species with the first-order rate constant k_1 , and $(1 - \theta_1)$ is the fraction with k_2 . The rate constants (k_1 and k_2) did not vary much with H-content: $k_1 \approx 1.3 \text{ ps}^{-1}$ in O₂ and 0.2 ps^{-1} in H₂O, and $k_2 \approx 0.012 \text{ ps}^{-1}$ in O₂ and 0.015 ps^{-1} in H₂O (see Tables S1 and S2). In contrast, the fraction of highly reactive species (θ_1) was found to decrease as the H-content increased (Figure 4c,f).

Figure 4b,e plots the total bond order (TBO) distributions of carbon atoms that reacted with O₂ and H₂O, respectively. In the TBO histograms, the population of TBO = 4 is zero because fully coordinated carbon atoms never react with O₂ or H₂O and therefore are not included in the calculation. Qualitatively, these results suggest that the relative population of extremely under-coordinated species decreases as the H-content in a-C:H increases, which could be correlated with the decrease in θ_1 . To show this correlation, we plotted the fraction of atoms with TBO < 3 in Figure 4c,f. Although this cutoff value for TBO is somewhat arbitrary (plots with different cutoff values are shown in Figure S10), the general trend found here is that a-C films with a higher H-content have a smaller fraction of highly reactive carbon species (θ_1) and a lower population of extremely under-coordinated carbon species. These trends observed in reactive MD simulations

with a-C:H may explain the lower oxidation probability of 40-HDLC as compared to 30-HDLC (Figure 3).

3.4. Removal of Oxidation Products by Frictional Shear. In addition to the oxidation reaction probability of the surface in each environmental condition, the Langmuir-type reaction kinetics analysis of COF also provided the removal probability (γ) of oxidation reaction products upon frictional shear at the steady state. Figure 5a plots the removal probability of oxidized species by friction (γ^{O_2} and $\gamma^{\text{H}_2\text{O}}$) as a function of partial pressure of O₂ and H₂O in the gas environment in which the friction test was conducted. In humid conditions, both $\gamma_{30\text{-HDLC}}^{\text{H}_2\text{O}}$ and $\gamma_{40\text{-HDLC}}^{\text{H}_2\text{O}}$ decreased as the partial pressure of water vapor ($P_{\text{H}_2\text{O}}$) increased (i.e., as RH increased). This could be due to the lubrication effect of physisorbed water molecules.^{67,68} However, in the O₂ environment, $\gamma_{30\text{-HDLC}}^{\text{O}_2}$ and $\gamma_{40\text{-HDLC}}^{\text{O}_2}$ exhibited opposite trends.

The partial pressure dependences of $\gamma^{\text{H}_2\text{O}}$ and γ^{O_2} appeared to correlate with the wear rate of HDLC. Figure 5b plots the wear volume, normalized by the sliding distance and the applied force, of 30- and 40-HDLC films versus P_{O_2} and $P_{\text{H}_2\text{O}}$. The wear rate of 30-HDLC in dry N₂ was quite high because defect sites exposed by friction were not hydrogenated enough probably due to the lower H-content in the film (Figure 2a).¹⁴ In low partial pressure of H₂O, the 30-HDLC wear rate was still high, which was probably due to insufficient coverage of the physisorbed water layer. At $P_{\text{H}_2\text{O}} \approx 0.4 \text{ kPa}$, where the adsorbed water forms almost complete monolayer,⁶⁹ the wear rate was three orders of magnitude smaller than that in low humidity conditions ($\text{RH} \leq 8\%$). Upon further increase of $P_{\text{H}_2\text{O}}$, the wear rate of 30-HDLC continued decreasing. In the case of 40-HDLC in the $\text{RH} \geq 2\%$ condition, the wear rate did not increase even though the COF was much larger than the 0% RH case. The wear rate of 40-HDLC decreased at high RH condition, which was consistent with the decrease in $\gamma_{40\text{-HDLC}}^{\text{H}_2\text{O}}$ (Figure 5a).

In the O₂ environment, the 40-HDLC wear rate gradually increased as P_{O_2} increased (Figure 5b), again consistent with the $\gamma_{40\text{-HDLC}}^{\text{O}_2}$ trend in Figure 5a. In the case of 30-HDLC, the wear rate decreased rapidly at $P_{\text{O}_2} = 4.0 \text{ kPa}$ (which is one-fifth of the atmospheric O₂ concentration) and then continued decreasing as P_{O_2} increased further.

3.5. Implication to O₂ Partial Pressure Dependence of HDLC Friction. The α^{O_2} and γ^{O_2} obtained in this kinetics study can provide new insight into the distinct frictional behavior of 30- and 40-HDLC in oxidizing environments. Figure 6 shows the steady-state COF of 30- and 40-HDLC after the run-in period in various partial pressures of O₂. The large COF difference between 30- and 40-HDLC at low P_{O_2} gradually decreased as P_{O_2} increased. When P_{O_2} was higher than 4.0 kPa (the yellow-shaded region), 30- and 40-HDLC had quite similar COFs at the steady state. However, the kinetics analysis with the Langmuir-type reaction model suggested a noticeable difference in the fraction of O₂-oxidized components in the sliding track ($\theta_{\text{ss}}^{\text{O}_2}$; see Figure S5c). Since the surface chemistry is dynamically changing during the sliding contact and between two consecutive sliding cycles, both the oxidation reaction probability (α^{O_2} ; Figure 3) and the material removal probability (γ^{O_2} ; Figure 5a) must play important roles. The net effect of α^{O_2} and γ^{O_2} might have resulted in convergence of the effective shear stress of 30- and

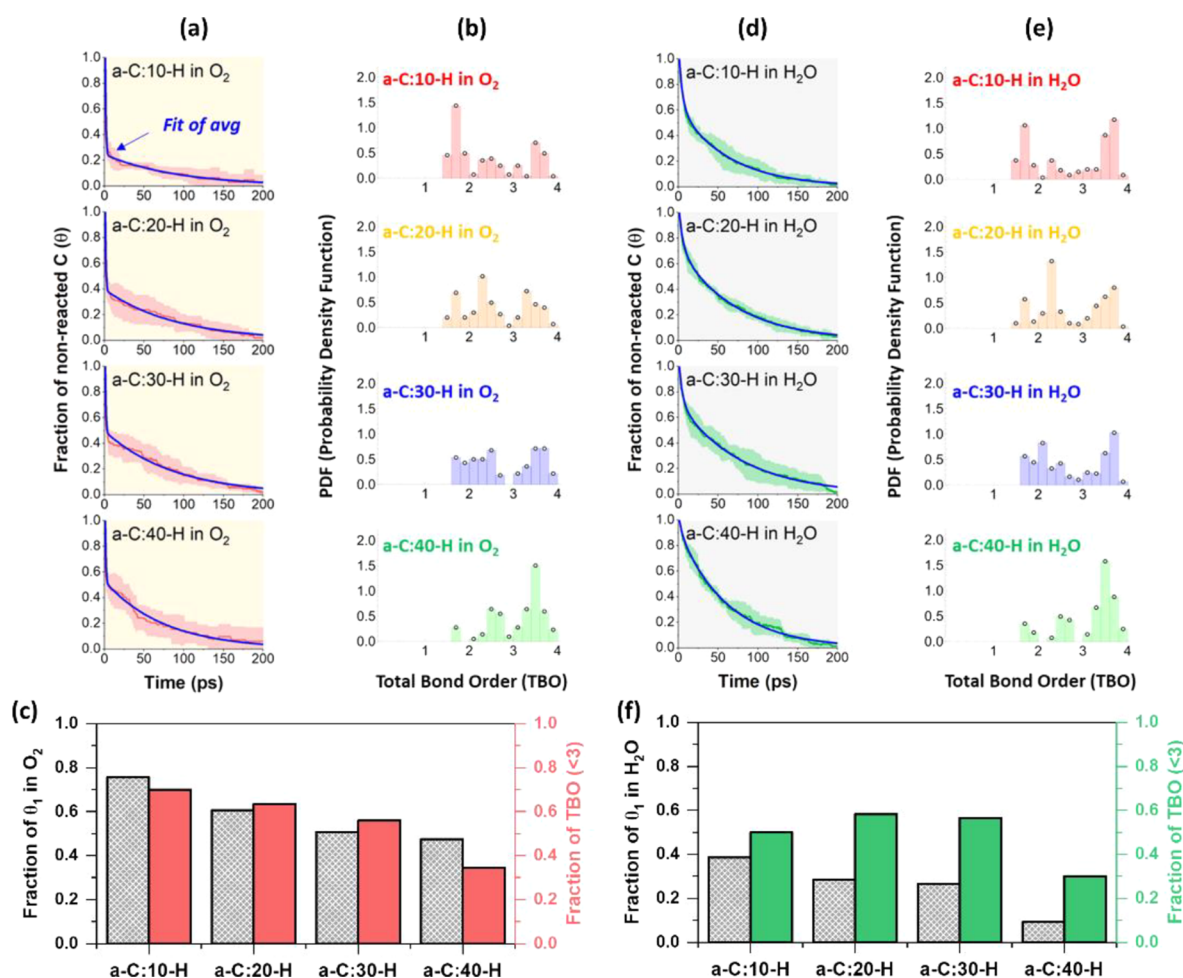


Figure 4. Simulation-calculated evolution of the fraction of yet-to-be reacted carbon atoms (θ) of various a-C films as a function of time during reactions with (a) O_2 and (d) H_2O molecules. The histogram of the total bond order (TBO) of the reacted carbon with (b) O_2 and (e) H_2O molecules. Comparison of the fraction of highly reactive carbon atoms (θ_1) to the fraction of carbon atoms with TBO < 3 of various a-C films in (c) O_2 and (f) H_2O conditions. The results from individual simulations corresponding to (a) and (d) are shown in Figure S9. The relative population of TBO in (b) and (e) was depicted using the probability density function, representing the probability distribution of TBO in a histogram where the height of each histogram bar multiplied by the width of the TBO bin size is unity.

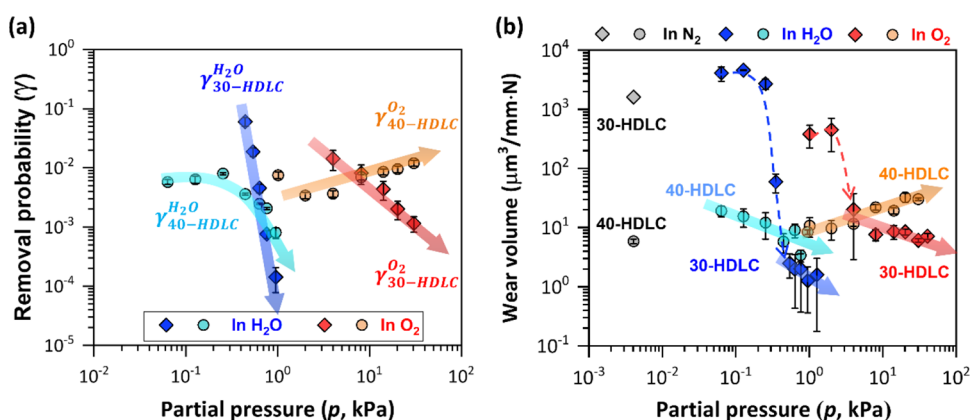


Figure 5. (a) Removal probability of re-oxidized species at the 30-HDLC and 40-HDLC surface upon frictional sliding as a function of partial pressure of H_2O and O_2 ($P_{\text{H}_2\text{O}}$ and P_{O_2}) obtained with the Langmuir-type kinetics equation.²⁵ All the data of 40-HDLC were excerpted from our previous study.²⁵ (b) Wear volume of 30- and 40-HDLC in dry N_2 and various partial pressure of H_2O vapor and O_2 gas measured with 3D optical profilometry. In N_2 and low partial pressure of H_2O and O_2 , 30-HDLC showed high wear. The friction data were reproducible, as can be seen in Figures S4 and S8.

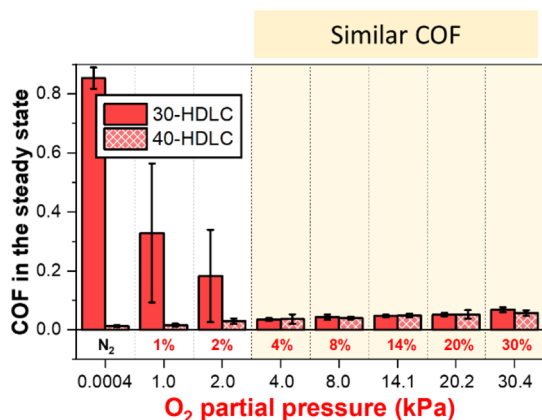


Figure 6. COF of 30- and 40-HDLC in the steady state in various partial pressure of O_2 gas. The steady-state COF values of 30-HDLC in $P_{O_2} > 4.0$ kPa were reproducible, as shown in Figure S5 (see our previous study²⁵ for the reproducible COF data of 40-HDLC).

40-HDLC films in $P_{O_2} > 4.0$ kPa. This argument is based on the fact that the contact areas were similar (see Section 2.2).⁴⁰ The individual contributions of α^{O_2} and γ^{O_2} to COF could not be determined in the current study.²⁵

3.6. Implications to Relative Humidity Dependence of HDLC Friction. In low humidity ($RH < 14\%$), the steady-state COF of 30-HDLC was much larger than that of 40-HDLC (Figure 7a). This must be due to incomplete coverage of the 30-HDLC surface with water and the intrinsically high COF of 30-HDLC (see COF of 30-HDLC in dry N_2 ; Figures

2a and S4b). In $RH \geq 14\%$, where the surface was fully covered with an adsorbed water layer⁶⁹ (and oxidized due to reactions with water; Figure S5c), 30-HDLC exhibited a lower COF than 40-HDLC (Figure 7a). The adsorbed water molecules can provide the vapor phase lubrication (VPL) effect;^{67,68} if the lubrication effect of the adsorbed water layer is similar regardless of the H-content in the HDLC bulk, then the cause for this difference in COF must be something else.

In a previous study on the RH dependence of 40-HDLC,⁴³ it was found that the SS counter-surface undergoes galvanic corrosion when the sliding interface is transformed into the graphitic structure (so becomes electrically conductive) and the adsorbed water layer is thick enough to act like an electrolyte. Supporting this argument, Raman analysis of the transfer layers (Figure 7b,c) showed the presence of iron oxide particles such as hematite (Fe_2O_3) and magnetite (Fe_3O_4) at high RH conditions, which must be due to galvanic corrosion of the SS counter-surface. The presence of these particles could cause reduction of the real contact area, which may lower the sliding friction. The Raman analysis (Figure 2b) found that the degree of graphitization is larger for the 30-HDLC surface than that for the 40-HDLC. Thus, the galvanic corrosion of the SS counter-surface would occur more readily on the 30-HDLC surface. In fact, SS corrosion was evident at RH 30% for the 30-HDLC surface, while it happened at RH 40% for the 40-HDLC surface (Figure 7c). In the previous study,⁴³ when galvanic corrosion of the SS counter-surface occurred, wear of HDLC was reduced. Interestingly, the same trend was observed in this study where, at high RH, the wear of 30-

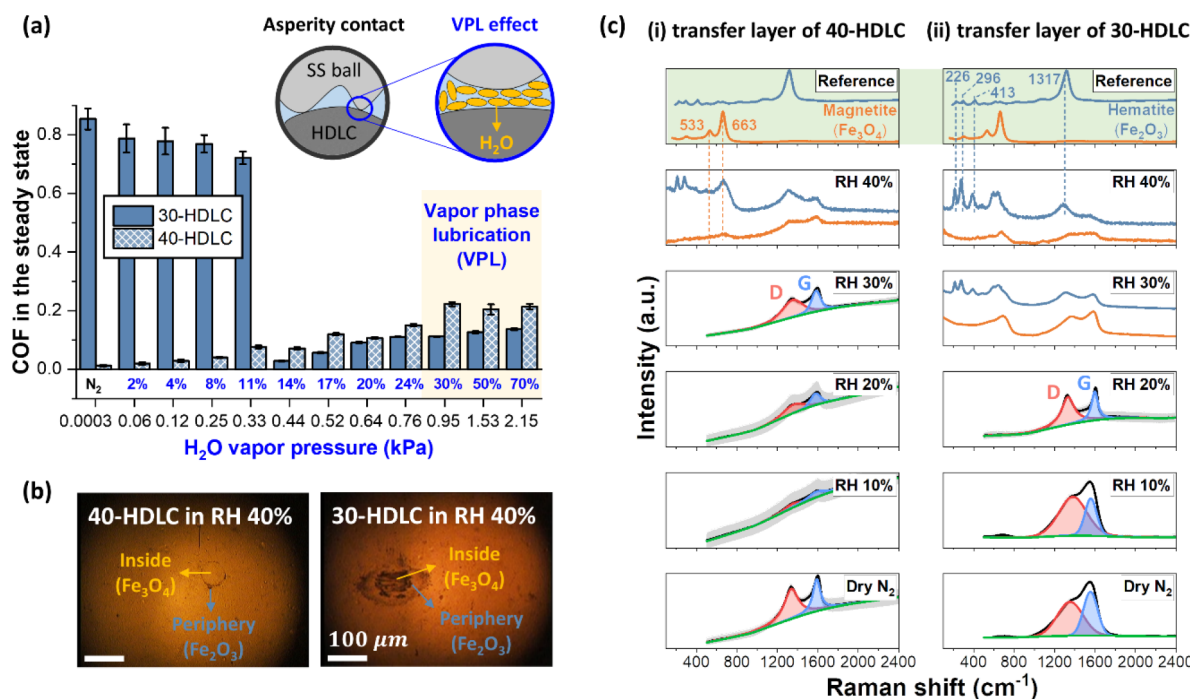


Figure 7. (a) COF of 30- and 40-HDLC at the steady state in various partial pressures of H_2O vapor. (b) Optical images of the transfer layers formed from 40-HDLC (left) and 30-HDLC (right) in RH 40%. (c) Raman spectra of the transfer layers formed from (i) 40-HDLC and (ii) 30-HDLC in dry and humid N_2 conditions. In (a), the inset depicts the vapor phase lubrication induced by physisorbed water molecular layers at the sliding interface at high humidity,^{67,68} and the yellow-shaded region corresponds to the boundary lubrication regime. Reproducible COF data of 30-HDLC in (a) can be found in Figure S5 (see our previous study²⁵ for the reproducible COF data of 40-HDLC). In (c), the green-shaded panels display the Raman spectra of magnetite and hematite as a reference. Magnetite and hematite were mostly found inside and near periphery of contact area, respectively (see Figure 7b).

HDLC was found to be lower than the wear of 40-HDLC (Figure 5b).

4. CONCLUSIONS

The effects of the HDLC film hydrogen content and of the gas environment on the lubrication performance of HDLC were studied by analyzing the transfer layers on the counter-surface as well as partial pressure dependence of friction and wear. Raman and XPS analyses of the transfer layer suggested that the shear plane of 30- and 40-HDLC exhibits shear-induced graphitization and surface oxidation in the tested condition. From the kinetics analysis of the friction data, it was found that the oxidation probability of HDLC with O₂ and H₂O molecules was extremely high, comparable to that of highly reactive catalysts. The 30-HDLC surface had a higher oxidation probability than the 40-HDLC surface. Reactive MD simulations suggested that the higher oxidation probability of HDLC with a lower H-content may be due to a larger population of under-coordinated carbon species. Overall, the interplay between the oxidation and removal probability and the degree of graphitization of the shear plane were shown to be important factors governing the distinct friction and wear behaviors of HDLC in oxidizing gas environments.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.3c05316>.

Detailed Raman analysis, contact angle measurements, and friction tests of HDLCs and transfer layers; tabulated Raman band parameters of HDLC films and transfer layers; detailed simulation-calculated temporal change of the fraction of yet-to-be-reacted carbon atoms (θ) of a-C:H films; and tabulated kinetic parameters of a-C:H films obtained from MD simulation (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Seong H. Kim – Department of Chemical Engineering and Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania 16802, United States; orcid.org/0000-0002-8575-7269; Email: shk10@psu.edu

Authors

Seokhoon Jang – Department of Chemical Engineering and Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania 16802, United States; orcid.org/0000-0002-9198-7853

Muztoba Rabbani – Department of Mechanical Engineering, University of California, Merced, California 95343, United States

Andrew L. Ogrinc – Department of Chemical Engineering and Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania 16802, United States

Maxwell T. Wetherington – Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania 16802, United States

Ashlie Martini – Department of Mechanical Engineering, University of California, Merced, California 95343, United States; orcid.org/0000-0003-2017-6081

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acsami.3c05316>

Notes

The authors declare no competing financial interest.

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