In situ transmission electron microscopy and scanning transmission electron microscopy studies of sintering of Ag and Pt nanoparticles

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Abstract

Transmission electron microscopy and scanning transmission electron microscopy studies were conducted in situ on 2–5 nm Pt and 10–40 nm Ag nanoparticles to study mechanisms for sintering and to measure relevant sintering kinetics in nanoscale particles. Sintering between two separated particles was observed to initiate by either (1) diffusion of the particles on the sample support or (2) diffusion of atoms or small clusters of atoms to the neck region between the two particles. After particle contact, the rate of sintering was controlled by atomic surface diffusivity. The surface diffusivity was determined as a function of particle size and temperature from experimental measurements of the rate of neck growth of the particles. The surface diffusivities did not show a strong size effect for the range of particle sizes that were studied. The surface diffusivity for Pt nanoparticles exhibited the expected Arrhenius temperature dependence and did not appear to be sensitive to the presence of surface contaminants. In contrast, the surface diffusivity for Ag nanoparticles was affected by the presence of impurities such as carbon. The diffusivities for Ag nanoparticles were consistent with previous measurements of bulk surface diffusivities for Ag in the presence of C, but were significantly slower than those obtained from pristine Ag.

Keywords: Microscopy; Diffusion; Kinetics; Coarsening; Densification

1. Introduction

Nanoparticles (NPs) possess unique properties stemming from their nanoscale dimensions and thus are of great interest in a wide variety of applications, such as textiles, renewable energy, the environment, health, electronics and agriculture. However, due to their large surface-area-to-volume ratio and large curvature, nanoparticles have a strong tendency to coalesce and sinter during processing or usage over short time scales and at low temperatures, which leads to significant changes in behavior and performance. In some applications, such as in catalysis, sintering is detrimental because it decreases catalytic activity, but in other applications such as electrical interconnects, these changes are beneficial because they enhance conductivity. In either case, understanding the mechanisms and measuring sintering kinetics at temperatures experienced by NPs are critical for controlling material properties.

The influence of particle size and temperature on sintering of micron-sized particles has been previously studied and simple scaling models such as Herring’s law have been developed to predict the influence of particle size on sintering kinetics \cite{1}. However, there are several complications in utilizing such predictions: (1) sintering models require

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experimental data in the appropriate temperature and particle size regimes. In the case of diffusion data, there is a paucity of data at low temperatures that are relevant to NPs. (2) Experimental studies on NPs often show discrepancies between these predictions made from data obtained at high temperatures and for larger particle sizes [2,3]. (3) Theoretical models have traditionally been evaluated by comparison with experimental observations of sintering in powder ensembles containing a distribution of particle sizes that were obtained by postmortem characterization [4–10]. However, discrepancies between the experimental observations and the model predictions have caused debate about the interpretation of indirect observations to study sintering processes [7,11].

The use of in situ transmission electron microscopy (TEM) techniques that are capable of monitoring dynamic processes in individual nanoparticles in real time can resolve the uncertainties that arise from postmortem experiments. Previous in situ TEM experiments [12–24] used a miniature furnace with a heating coil to indirectly heat the sample, while temperature was measured with an attached thermocouple. Indirect heating results in substantial thermal drift, making it difficult to perform these experiments at high magnifications. Furthermore, it typically takes several minutes for this type of furnace to ramp to the observation temperature, and thus sintering occurs during heating and before the temperature has stabilized. Finally, some sintering experiments have been performed using a focused electron beam in the transmission electron microscope to directly heat the sample. For these experiments, the temperatures were estimated from the beam current density and irradiation time. However, we have recently shown that temperatures cannot be accurately determined for individual nanoparticles from these experiments unless the contact angle between a specific particle and substrate is known [25]. Together these effects make it very challenging to perform quantitative sintering studies on small nanoparticles.

To address the aforementioned issues, we use a novel heating stage that is capable of rapidly heating the sample with minimal thermal drift so that high resolution imaging can be performed. In this study, we focus on two face-centered cubic (fcc) metals, Ag and Pt, and compare their sintering behaviors. Two types of samples were studied: (1) commercial NPs that contain ubiquitous carbon on their surfaces; and (2) specially prepared NPs produced in our laboratory that did not have organics intentionally added on the particle surface. The influence of particle size, temperature and surface condition are studied by observing sintering in real time using TEM and scanning transmission electron microscopy (STEM) and measuring the rates of sintering in the two particle systems. From these data, the surface diffusivities are determined and compared to previous measurements made on bulk materials.

2. Experimental procedure

2.1. Materials and sample preparation

Three types of samples prepared from commercially available nanoparticles were studied. Ag NPs with nominal mean sizes of 15 and 40 nm were obtained from Nanotechnologies Inc. (Austin, TX). These NPs were synthesized using a pulsed-plasma, dry synthesis method that resulted in carbon deposited on the surfaces of the Ag NPs. Another set of samples consisted of Pt NPs (Johnson Matthey Technology Centre, Oxfordshire, UK) with a nominal size of either 2 nm or 6 nm that were deposited onto a strongly adhering particulate carbon support (Ketjen, Tokyo, Japan). A third set of samples consisted of Pt NPs with a mean size of 2.8 nm (Tanaka Kikinzoku Kogyo, Tokyo, Japan) that were deposited onto weakly adhering carbon (Vulcan, Cabot, Boston, MA) particles. TEM samples were prepared by first dispersing the NP samples in ethanol and then ultrasonicitating for 10 min to reduce particle agglomeration. A drop of the suspension was then deposited onto the TEM heater chip and the liquid was evaporated.

2.2. In situ TEM/STEM heating and characterization

In situ heating experiments were performed in both conventional bright field (BF) TEM mode using phase contrast imaging and in high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) mode using Z-contrast imaging. The TEM experiments were performed in a JEOL 2010F TEM operated at 200 keV, while the STEM experiments were conducted using a JEOL 2200FS STEM/TEM or a JEOL JEM-ARM 200F, both operated at 200 keV. Compared to conventional phase contrast imaging in a TEM, the aberration-corrected STEM offers superior resolution, allowing imaging of very small NPs, atomic clusters and even single atoms. The HAADF images were obtained from a probe with a convergence angle of 25 mrad, and electrons scattered at angles ranging from 100 to 170 mrad. As a result the HAADF images contain nearly zero diffraction contrast and provide essentially mass-thickness contrast. Thus, HAADF imaging is a powerful technique for observing the coalescence process, particularly in the neck region between sintering particles, where there can be significant variations in thickness.

The NPs were heated in situ using an Aduro™ heating stage (Protochips Inc., Raleigh, NC) [26]. This heating stage uses a disposable micro-electro-mechanical system (MEMS) device that serves both as the specimen support grid and the heating element with an electrical feedthrough that connects to an external power supply. The device consists of a 150 nm thick, 500 μm × 500 μm, freestanding membrane made from a conductive ceramic material that is suspended over a 4 mm × 6 mm silicon
chip. For electron transparency, the ceramic membrane is patterned with a series of 6 μm diameter holes, which are subsequently overlaid with a holey carbon film which supports the NPs. Joule heating occurs when current is forced through the ceramic membrane and is used to control the temperature. The current vs. temperature response of each device is calibrated at the factory using an imaging pyrometer in a vacuum probe station at a pressure similar to what is used in a TEM column. Unlike conventional heating holders, this heating stage is capable of very fast heating rates up to $10^6 \text{C}^\circ \text{s}^{-1}$ with extremely low drift, even at high temperatures. This allows isothermal sintering experiments to be carried out in the TEM, since heating to the desired sintering temperature can be achieved nearly instantaneously. The in situ heating experiments were performed at temperatures from 25 to 500 °C in order to investigate the effects of size and temperature on sintering of NPs. The size and temperatures for each experiment were chosen such that the sintering process could be observed in situ within a reasonable time frame.

The accuracy of the temperature measurements for the as-received heater chips was assessed using a known solid-to-vapor phase transformation. Details of this procedure are presented elsewhere [25]. Our experiments revealed temperature discrepancies of between 20 and 150 °C between the apparent and actual temperatures that were attributed primarily to beam heating of the particles. The large range in the temperature discrepancies is believed to arise from variations in the contact area between individual particles and the TEM heater substrate, which leads to point-to-point variations in heat transfer rates between the NPs and the TEM substrate. The beam heating effects and point-to-point variations in temperature results in significant but quantifiable error bars on our temperature measurements during the in situ heating experiments.

2.3. Determination of sintering parameters

During the early stages of sintering, neck growth occurs to reduce the large chemical potential at the particle contact points where the neck radius is very small. Possible mass transport mechanisms for neck growth include grain boundary diffusion, surface diffusion and lattice diffusion, as well as plastic deformation. For NPs, it is unlikely that dislocation-driven plastic flow would contribute significantly to neck growth in fcc NPs given the large stresses required for plastic flow [27]. Surface diffusion is the dominant mass transfer mechanism at lower temperatures, as shown by the experiments of Kuczynski [28], but this is especially so for small particles that have larger surface-atom-to-volume atom ratios. The surface diffusivities for fcc metals at low temperatures are typically many orders of magnitude larger than the other diffusivities [29].

For surface diffusion, the change in neck radius, $t$ for a given particle radius, $a$ and temperature, $T$ is given by [28,30]

$$X^2 = \frac{56 \Omega a^3 \gamma_s D_s \delta t}{kT} \quad (1)$$

where $\Omega$ is the atomic volume, $\gamma_s$ is the surface energy, $D_s$ is the surface diffusivity, $\delta$ is the surface diffusive width and $k$ is Boltzmann’s constant. From our sintering experiments and using Eq. (1), $D_s$ for NPs was determined by measuring $x$ and $a$ as a function of time at a given temperature, since all of the other parameters are known.

The measurements of the particle geometry relevant to sintering were performed using DigitalMicrograph™ software (version 1.7.138, Gatan Inc. Pleasanton, CA). NPs were selected, such that they were nearly spherical (i.e. the major and minor axes were within 5% of each other), so that a two-particle sintering model could be used to determine the sintering parameters. To measure $a$, the edges of the NPs were first detected and a circle was fit to each NP using a Matlab® routine [31] that computed a least-squares fit for a circle with a set of $(x,y)$ coordinates selected on the edges of the NP. The area of the fitted circle was used to obtain an equivalent particle radius for a spherical NP. The neck radius was calculated from one-half the length of a line drawn perpendicular to the intersection of the two particles. Examples of measurements of $a$ and $x$ are shown in Fig. 1.

3. Results

3.1. Sintering between two NPs

Fig. 2 shows a representative sequence of TEM images taken at 400 °C that shows sintering between two 40 nm NPs that were produced by combustion synthesis. As the two NPs contact each other, there is rapid growth of the neck in the subsequent 3 min before the rate of neck growth slows over the subsequent 12 min. Note also that there is clearly some carbon present on the surface of the NPs that is most apparent in the first frame (indicated by the arrows).

Contrast changes are also apparent in the NPs from frame-to-frame. For example, the particle on the left, which is bright in the initial frame, darkens after 3 min and then brightens after 8 min. Contrast changes such as these could be due to either rotations of the NPs or the movement of the carbon support on which the particles are suspended, effectively rotating the particles with respect to the electron beam. In addition, we see unusually bright contrast around the edges of the NP on the left. Such contrast has been attributed either to the presence of a liquid phase on the particle surface or variations in thickness around the edge of the sample [32]. An analysis of the melting temperature as a function of particle size suggests that the melting temperature for these particles is at least 940 °C [33]. Since the temperature at which this experiment was conducted was well below the melting temperature of the Ag NPs, the contrast changes must be due to thickness variations.
Another sequence of in situ TEM images, presented in Fig. 3, shows a second type of behavior that was observed in some of the sintering experiments where the onset of sintering was activated by a third particle. In this case, the sequence was taken at 200 °C and shows two 15 nm silver NPs that contain twins, which are common for Ag particles in this size range. The particles are initially separated by a small distance before contact between the NPs is initiated by the motion of a third particle. At this point, sintering occurs by rapid neck growth. As the dihedral angle approaches the equilibrium value of 161° [34] after ~15 min, motion of the grain boundary between the particles begins. In addition, the smaller NP at the bottom of the frame appears to move towards the two NPs sintering in the middle of the frame and eventually coalesces with the larger NPs after some time.

Contrast changes are also apparent in the NPs shown in Fig. 3 from frame-to-frame. To further study the cause of these changes, fast Fourier transforms (FFTs) were taken for each of the images shown in Fig. 3. The diffraction data obtained from the FFTs are shown in Fig. 4. This sequence shows that the FFT patterns change from frame-to-frame, confirming that particle rotation occurs during sintering. For example, the particle goes from a near two-beam
condition at 13 min to a near zone axis condition at 17 min. These rotations are on the order of a few degrees since they are all in the same zone axis.

3.2. Sintering between many NPs

It is important to determine if the mechanisms for sintering that were observed in two particle systems are also active for the more realistic case of sintering between many NPs. Fig. 5 shows a sequence of in situ TEM images taken at 100 °C of multiple Pt NPs with a mean size of 6 nm. The particles have been labeled A–D. Particles B and C initially appear to be in contact with one another while particles A and D are isolated from the other particles. After 5 min, particle A migrates towards particle B and particle D migrates towards particle C. The particles were monitored for 16 min and very little neck growth was observed between particles A and B after the initial contact. Particles C and D move towards each other but do not appear to contact. After 9 min particles B and C appear to move apart without sintering.

There are at least two possible explanations for the observed behaviors: (1) the NPs may be mobile on the support and coalesce only when they make contact or, if they are not in the same plane, they may simply move past each other with their projections appearing to overlap; (2) the entire carbon support on which the particles are suspended may move due to differential heating. To distinguish which of these phenomena are responsible for the observed behavior, HAADF STEM imaging was employed. Fig. 6 is a sequence of HAADF STEM images showing sintering of 2 nm platinum NPs at 500 °C that are labeled 1–11. There is clearly relative motion between the particles, as seen from the changes in positions of the particles with time. For example, particles 5 and 6 move toward each other and sinter while particles 9 and 10 drift apart. It is not likely that substrate motion is responsible for the apparent relative motion between particles since their motion appears to be random. Motion of the carbon support would cause correlated motions between the particles, unless the magnitudes of the perturbations of the surface were of the order of the size of the NPs, which is not plausible given the size scales observed here.

It is also interesting that particles 9 and 11 in Fig. 6 disappear from the support with little or no motion on the support. Wen et al. have postulated that Ag NP mass

Fig. 3. A sequence of in situ TEM heating images showing sintering of two 15 nm Ag NPs at 200 °C.
transport can occur by evaporation–condensation, where Ag atoms evaporate into the vapor and the re-condense on another nanoparticle [35,36]. The mechanism for the change in particle size was investigated further by performing additional higher resolution in situ HAADF STEM experiments on 2 nm Pt NPs at 300 °C (Fig. 7). The NPs are initially completely separated from each other. However, after ~20 min they make contact and sinter via neck growth. We observe that the mass transport does not occur by evaporation, but rather by surface diffusion along the carbon support. At this scale, single atoms and small clusters of Pt are clearly visible between the NPs and they appear to be mobile on the substrate. This clustering of atoms between the particles leads to the formation of bridges between the NPs and, once contact is made, the neck begins to grow. The source of these atoms is likely small clusters or even individual atoms that are deposited onto the support surface and then diffuse due to thermal activation from both the heating stage and the electron beam. The atoms and clusters appear to be mobile on the surface until they condense onto the surface of an existing particle. This dissolution–condensation mechanism is analogous to an Ostwald ripening process that occurs in liquids. Note, however, that we do not see the expected behavior of larger NPs growing larger that is expected from traditional Ostwald ripening. Rather, sintering appears to be favored for larger NPs that are mobile on the carbon support, while the Ostwald-ripening-like process appears to be favored for smaller NPs that are immobile on the carbon support. These experiments indicate that for many particle systems, ripening as well as sintering may occur simultaneously. Lastly, a comparison of the results at 100 and 500 °C suggest that atomic/cluster surface diffusion and ripening are more likely to occur at higher temperatures. These in situ experiments reveal a mechanism for sintering of NPs where atoms and small clusters present on the substrate can play a major role in initiating sintering of NPs.

4. Analyses of sintering data

A number of in situ experiments similar to those shown in Figs. 1–7 were conducted with Ag and Pt particles with a range of particle sizes and at a range of temperatures. The
Fig. 5. A sequence of in situ TEM heating images of 6 nm Pt NPs on a carbon support at 100 °C, showing particle migration and/or motion of the carbon support.

Fig. 6. In situ STEM images of 2 nm Pt NPs at 500 °C, showing that sintering can occur by both particle migration and coalescence as well as Ostwald ripening.
measured values of neck size with time were measured from these experiments and used to calculate the surface diffusivity using Eq. (1). The surface diffusion coefficients, $D_s$, for silver NPs with size ranges from 12 to 40 nm and at temperatures of 200–400 °C are shown in Fig. 8. The values of $D_s$ were found to be in the range $4.2 \times 10^{-16}$ to $1.1 \times 10^{-20}$ cm$^2$ s$^{-1}$. Given the error bars in measuring temperature, there does not appear to be a statistically significant NP size effect on surface diffusivity for NPs in the size ranges that were measured.

Fig. 8 also shows previously reported values of surface diffusivities for bulk silver and thin films of silver obtained under different conditions and at different temperatures. The most comprehensive surface diffusivity data for Ag have been obtained from bulk measurements at temperatures above $0.5T_m$ [37] because the kinetics are too slow to observe experimentally using this technique at lower temperatures. Thus, to compare bulk measurements to the current results, it is necessary to extrapolate the bulk $D_s$ to temperatures below $0.5T_m$ using an Arrhenius relationship (shown as a dashed line in Fig. 8). It is recognized that such extrapolations may not be valid because the fundamental mechanisms of diffusion can change with temperature (as occurs in bulk Ag at ~500 °C). In addition, small uncertainties in the high temperature data can lead to large errors when extrapolated to low temperatures. Although caution is warranted when making quantitative comparisons between data with large uncertainties, it is nevertheless clear that the measured surface diffusivities from this study are several orders of magnitude lower than previously reported bulk values.

Surface diffusivities have also been measured previously from the motion of atomic clusters of Ag using scanning tunneling microscopy (STM) in ultra-high vacuum for clusters deposited on thin films of silver. These room-temperature diffusivities for clusters range from $10^{-15}$ to $10^{-18}$ cm$^2$ s$^{-1}$) [35,36,38]. Pai et al. have suggested that the diffusivities for clusters follow a power law with respect to the cluster size with an exponent of 2.28 for Ag [38]. Using their data and extrapolating to a single atom of Ag, we obtain $D_s = 8.8 \times 10^{-20}$ cm$^2$ s$^{-1}$. This is significantly lower than the values obtained from bulk silver at...
obtained. Assuming an Arrhenius dependence on temperature, the sensitivity of $D_s$ to temperature can be estimated by plotting $\Delta \log D_s$ vs. $\Delta T$ for the ranges of temperature used in our experiments (Fig. 9). For these calculations, we used the previously reported values of the diffusivity prefactor, $D_0$ (1.6 x 10^{-11} cm^2 s^{-1}), and activation energy for surface diffusion, $E_D$ (0.4 eV), obtained from STM measurements on silver [100] surfaces [39]. For a temperature error of 150 °C, the resulting error in diffusivity is less than an order of magnitude, which is relatively minor compared to the variations in diffusivity that have been reported in the literature. Thus, the temperature uncertainty due to electron beam heating cannot explain the large discrepancies in the measured values of surface diffusivity for Ag.

A more likely cause of the large scatter in the bulk diffusivity data for Ag and for the discrepancies between the data can be related to differences in sample surface conditions. The activation energy for surface diffusion, $E_D$, for thin films of silver obtained from STM [40] and spot-profile analysis of low energy electron diffraction [41] experiments performed in ultra-high vacuum, are significantly lower than the $E_D$ values obtained from resistivity measurements on thin, {111} oriented films of silver in air [42]. This suggests that the environment plays a major role in the sintering process and that the presence of oxides or other adsorbed species on the surface of the NPs can retard the sintering of the NPs. We have shown that the presence of carbon on the surfaces of Ag NPs can significantly retard sintering [43] and our experiments with Ag NPs in which we reduced the amount of carbon present on the Ag surfaces showed a significant increase in the diffusivities. For example, for a 40 nm NP at 400 °C, the surface diffusivity was determined to be 1.2 x 10^{-14} - 1.8 x 10^{-14} cm^2 s^{-1}, which is two orders of magnitude greater than the value we obtained for the same size particles at the same temperature, but where there was significant carbon surface coating [43]. In STEM studies of diffusion Ag clusters, Wen et al. also found that the diffusivity of Ag was significantly retarded in the presence of contaminants [35]. Thus, diffusivities obtained in the presence of carbon deposits on Ag NPs are not intrinsic surface diffusivities, but rather are effective diffusivities. This is a very important point, since most commercially available NPs usually contain some form of hydrocarbon added to prevent particle agglomeration. These hydrocarbons pyrolyze during sintering, resulting in carbon residue on the particle surfaces that can affect subsequent sintering if it is not fully oxidized. These results are also consistent with measurements obtained from silver deposited on pyrolytic carbon [44] that show significantly lower values of $D_s$ than for pure bulk silver. The values of diffusivity in this Ag/C system (10^{-16} - 10^{-12} cm^2 s^{-1} in the temperature range of 450–800 °C), when extrapolated to low temperatures, agree well with our measurements (Fig. 8).
clusters on the support towards the neck region or (3) motion of the support due to differential heating caused by the electron beam. Atomic or cluster migration are mechanisms for activation of sintering between two larger particles that have not been previously reported. These results demonstrate that the diffusion of small clusters of atoms on the support may affect the sintering of larger NPs by forming a bridge in between the NPs, which then leads to subsequent neck growth.

The values of $D_s$ (4.2 × 10^{-16}–1.1 × 10^{-20} cm^2 s^{-1})$ that were obtained from in situ sintering experiments on Ag NPs were significantly lower than values extrapolated from higher temperatures and were also lower than the values obtained from thin Ag films measured in ultra-high vacuum at room temperature using STM. Consistent with previous measurements of surface diffusivity, our results suggest that surface species are a likely cause for this discrepancy because the presence of carbon on the surface of NPs can significantly inhibit sintering in NPs. The effective diffusivities that were measured for Ag NPs with carbon surface coatings match well with reported values of diffusivity of silver in pyrolytically deposited carbon.

In contrast to the results obtained for silver, the values of $D_s$ measured for Pt are in close agreement with reported bulk values extrapolated from high temperatures and measurements performed at room temperature. This is believed to be due to the fact that platinum, being less reactive than silver, is less susceptible to contamination and also appears to be less susceptible to impurity effects on surface diffusion.

Electron beam heating effects result in a 20–150 °C increase in temperature over the temperature measured without the beam. The large range in temperatures caused by beam heating results from variations in beam current, NP size and, most importantly, the contact area between the NP and the substrate upon which the NP rests. This range results in some uncertainty in the temperature during our experiments and a corresponding uncertainty in the surface diffusivity, which was determined to be at most one order of magnitude. While this level of uncertainty is great enough that small variations in diffusivity cannot be determined using this technique, it is reasonably accurate compared to the large range in measured surface diffusivities that have been reported in the literature for silver. Within the accuracy of the measurements, we did not observe a statistically significant effect of particle size on the surface diffusivity of silver, which suggests that such an effect is relatively small over the range of NP sizes that were measured (for Ag, 12–40 nm).

5. Conclusions

The sintering of silver and platinum NPs was studied using a novel heating holder for in situ TEM/STEM heating experiments. Two mechanisms were observed for sintering in NPs: (1) a surface Ostwald-ripening-like process in which atoms or clusters dissolve onto the substrate surface and then are transported to and deposit onto another particle, or (2) particle migration along the surface, contact between the particles and coalescence. The Ostwald ripening process was found to be more prevalent at higher temperatures. For coalescence, it was found that contact between NPs can be initiated by (1) diffusion of the particles on the support, (2) migration of single atoms and small

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**Figure 10.** Plot of surface diffusivity vs. temperature for Pt. Data from the literature taken from Refs. [45–48]. The dashed line is an extrapolation of high temperature bulk Pt measurements to lower temperatures.

1.5 × 10^{-20}–6.5 × 10^{-20} cm^2 s^{-1} from our measurements obtained from sintering. Fig. 10 shows a comparison of these values with measurements from other experiments at or near ambient temperature on 300 nm thick Pt nanosheets on graphite (10^{-15}–10^{-16} cm^2 s^{-1}) [45], Pt single atoms on Pt {110} surfaces (3.16 × 10^{-19} cm^2 s^{-1}) [46] and columnar structured Pt electrodes (1.13 × 10^{-19} cm^2 s^{-1}) [47]. Also shown on this plot are data obtained from bulk Pt at high temperature [48], with the corresponding exponential extrapolation to room temperature. This plot shows that diffusivity values obtained in the current study are in general agreement with the diffusivities obtained from previous work. It is notable that unlike Ag, which shows wide range in the values of $D_s$ due to differences in surface condition, there is little discrepancy in the values of $D_s$ for the more noble Pt, even when it is obtained using different surface conditions and techniques.

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References