The recent developments in the manufacturing of advanced interconnects have largely centered on the Cu/low-k technology, where the processing challenges are coupled with those of material selection. The introduction of mechanically fragile low-k dielectrics has set strict limits on the usable down-pressure of chemical mechanical planarization (CMP) used in the processing of Cu interconnects. This in turn has driven the strategies for material removal more toward the chemical considerations of CMP, and less reliant on mechanical abrasion. At the same time, the CMP chemistries of the relatively unconventional new barrier materials have presented other challenges, because in the slurry environment, they often have appeared chemically too inert or too corrosive. If the CMP chemistries for these new materials are not properly controlled, the processed wafer can develop surface defects due to erosion and galvanic corrosion activated by the wet CMP process. Such defects are detrimental to device performance, and this issue is particularly relevant for the CMP of ultrathin (< 5 nm) barrier layers, where defect-control is often more critical than achieving high rates of material removal. Due to these reasons, the tasks of designing the slurry chemistries for metal CMP have become progressively more complex during recent years. This specific aspect of CMP consumable challenges can be addressed to a large extent by employing laboratory scale evaluations of slurry compositions with electrochemical measurements. The present work is based on this approach.

The role of electrochemical reactions (and hence the applicability of electro-analytical tests in this context) is integrated in the overall mechanism of chemically promoted metal-CMP. The commonly practiced CMP approach, the surface of the target metal is chemically prepared for low pressure planarization. The modified surface layers are composed of easily breakable oxides, hydroxides and/or other chemical complexes. During CMP, these layers are mechanically removed and chemically formed in a coupled fashion, which eventually leads to surface planarization. The interfacial reactions responsible for this process typically have mixed-potential origins, so that the apparently chemical reactions actually result from a combination of cathodic and anodic electrochemical steps. Identifying these reactions and understanding their responses to the tribological effects of polishing are essential to developing robust protocols for defect-control in CMP.

The electrochemical signatures of CMP specific surface reactions can be examined by using the techniques of open circuit potential (OCP) transients, potentiodynamic polarization (through linear sweep voltammetry, LSV) and electrochemical impedance spectroscopy (EIS). EIS can only be performed under strictly steady state conditions, and thus requires the exclusion of surface abrasion by abrasive particles and/or a polishing pad during such measurements. Nevertheless, steady-state EIS measurements can yield electrical equivalent circuit (EEC) models that are useful for probing the intrinsic CMP chemistry of a metal in the presence of various slurry components. The OCP and the polarization response characteristics of the metals considered for Cu/low-k interconnects generally exhibit strong response to tribological conditions, and depending on the polishing parameters used, can notably vary between the polishing and non-polishing situations.

The tribology-sensitive electrochemical features for metal-CMP systems contain a wealth of information about the formation and removal mechanisms of the CMP specific surface films. The detection and the analysis of these effects constitute a significant aspect of slurry engineering needed to develop new strategies for metal CMP. The experiments described here are based on these considerations, and are aimed at characterizing a specific slurry formulation intended for low-pressure planarization of Ru (a non-traditional barrier material, suitable as a substrate for direct electrodeposition of Cu without a seed layer), Ta (a conventional barrier metal) and residual Cu (standard wiring metal). Controlled tribo-corrosion is utilized as a strategy for chemically promoted CMP, and the slurry is designed to minimize the action of galvanic corrosion in the Ru-Cu and Ta-Cu bimetallic CMP systems.

The slurry used in this work contains sodium percarbonate (SPC, Na₂CO₃·1.5H₂O₂) and guanidine carbonate (GC, CH₃N₃·0.5H₂CO₃). The utility of SPC for stable solid-phase storage of H₂O₂ has been demonstrated previously. It has also been shown that the carbonate/bicarbonate anions (contained in SPC) can serve as efficient surface modifiers of Cu and Ta to facilitate low pressure CMP of these metals. Guanidine is broadly recognized for its surface complexing function in the contexts of Ru and Ta CMP. The carbonate salt of guanidine is chosen here to match the anion component of the other complexing agent, SPC, used in the experimental slurry. The OCP and polarization techniques are employed to bring out the effects of tribology on the electrochemical/chemical surface reactions, as well as to identify the associated reaction mechanisms. EIS measurements are performed to further explore these mechanisms.

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Theoretical Considerations

Mixed potential basis of CMP supporting reactions.— Metal surfaces submitted to CMP typically share the characteristic features of a mixed electrode, where the apparently chemical reactions originate from coupled activations of anodic and cathodic electrochemical steps.5,7 The protocol of data analysis involved in the present work centers on this mixed potential aspect of CMP. The details of this formalism are described elsewhere,6,18,19 and the following discussion briefly notes certain points that are relevant for the present analysis. Experimentally, the test metal is set up as a working electrode (WE) in a standard three-electrode configuration under tribo-electrochemical control. The surface reactions are allowed to occur at the OCP of the system, as well as by activation with an applied voltage, E.

The cathodic reactions in metal CMP typically constitute electrodereaction of oxidizers like H$_2$O$_2$ and/or O$_2$. The accompanying anodic steps correspond to corrosion reactions and surface complex formation. The cathodic reactions generally have higher Nernst potentials than those of the anodic steps, and can readily accept electrons from the latter. The net current (I) of the electrochemical reactions supported at the WE surface is: $I = I_a - I_c$, where $I_a$ and $I_c$ denote, respectively, the current contributions of the cathodic and anodic reactions in the given system. The equilibrium mixed potential ($E_{eq}$) corresponds to the open circuit condition of zero net current, with $I_a = I_c$. In general, $E_{eq}$ may be governed by multiple coexisting reactions, and the calculation of $E_{eq}$ for such a general case has been previously discussed.19 The essential features of this formulation are noted below by considering the mixing of a single cathodic reaction with a predominant anodic reaction. Under kinetic control of the given experimental system, $I_a = I_{a0} \exp[(E - E^0_a)/\beta_a]$ and $I_c = I_{c0} \exp[(E - E^0_c)/\beta_c]$, where $I_{a0}$ and $I_{c0}$ are the exchange currents of the principal cathodic and anodic processes, respectively.20 These exchange currents increase with increasing reactant concentrations, and are proportional to the associated reaction rate constants. $E^0_a$ and $E^0_c$ are the corresponding Nernst potentials, with $\beta_a$ and $\beta_c$ denoting the Tafel factors; $\beta_a = RT/(\alpha_a n F)$ and $\beta_c = RT/(1 - \alpha_a)nF$, where $n$ is the charge number of the faradaic process; $\alpha_a$ and $\alpha_c$ are the cathodic and anodic transfer coefficients, respectively. The $E_{eq}$ for this system can be evaluated by setting $E = E_{eq}$ in the condition, $I_a - I_c = 0$, and by using the above expressions of $I_a$ and $I_c$.

For the aqueous slurry solutions commonly used in CMP, it often is possible to take $\alpha_a \approx \alpha_c \approx 1/2$, and under this condition, the resulting expression for $E_{eq}$ has the following form:19 $E_{eq} \approx (1/2)[(E^0_a + E^0_c)/2 + \beta_1 \ln(I_{a0}/I_{c0})]$. $E_{eq}$ can be measured as the OCP of the system in a true zero-current setup, or alternately, as the corrosion potential ($E_{corr}$) by using LSV where a voltage dependent electrode current is activated during the experiment. Although both $E_{eq}$ and $E_{corr}$ represent the same $E_{eq}$ term defined above, the two separate taxonomies for this potential are commonly used to indicate their different measurement methods.

Anodic-cathodic selectivity of CMP reactions.— Corrosion-type mixed processes such as those found in the context of metal CMP are often characterized by experimentally detectable separate features of anodic and cathodic reaction zones.21–24 These reactions typically involve adsorbed intermediates, and due to their selective faradaic actions, the reaction sites can be classified as anodic or cathodic sites.25–28 The site-selective behaviors of such reactions can have a variety of origins, including short range electrostatic interactions, stability of adsorption geometry, site-distributed local work functions, presence of co-adsorbates, etc.29 This type of faradaic selectivity among corrosion sites also plays a role in the functions of a broad class of corrosion inhibitors that operate predominantly via site blocking, but instead of acting as mixed inhibitors, exhibit preferential suppression of anodic28,30 or cathodic24,32,33 reactions. Dissolution inhibitors from this category are often used in metal CMP slurries.

As shown by previous authors, the site-selective features of mixed reactions can be accounted for by relating $I_a$ and $I_c$ to the active areas of the associated reactions.30 In this approach, we write:

$I_a = i_a S_a$ and $I_c = i_c S_c$, where $i_a$ and $i_c$ are the inherent surface current densities of the cathodic and anodic reactions, respectively; $S_a$ and $S_c$ are the collective areas of the surface sites supporting the corresponding reactions. Similarly, $I_{a0} = i_{a0} S_a$ and $I_{c0} = i_{c0} S_c$, expressed in terms of the cathodic and anodic exchange current densities, $i_{a0}$ and $i_{c0}$ respectively. With these definitions,19

$$E_{eq} \approx \frac{E^{0_a} + E^{0_c}}{2} + \frac{\beta}{2} \ln \left( \frac{i_{a0} S_a}{i_{c0} S_c} \right), \tag{1}$$

where $\beta \approx \beta_a \approx \beta_c \approx 2RT/(nF)$.

Eq. 1 indicates how the surface modifying effects of CMP slurry additives could be manifested in the values of $E_{eq}$. Certain surface modifiers could affect the values of the individual Nernst potentials (e.g. by modifying the activity coefficients of the reaction products) and/or those of the exchange current densities (e.g. by altering the solvent reorganization energy at the reaction site). However, for typical surface-blocking/clearing type reactions of CMP, it is often possible to account for the observed changes in $E_{eq}$ in terms of the corresponding variations of $S_a$ and/or $S_c$. This latter mechanism also serves as a direct indicator of site-specific surface modifications. For instance, an anodic inhibitor would preferentially decrease the value of $S_c$, which, according to Eq. 1, would result in an upward shift of $E_{eq}$. Likewise, a cathodic inhibitor would decrease the value of $S_a$, and consequently send $E_{eq}$ to a lower value. Opposite effects of these would be introduced, by anodic and cathodic promoters, respectively. Since separate measurements of $S_a$ and $S_c$ are difficult, it is customary to express the electrode current density (i) as: $i = (I/S)$, which implies that

$$i = i_a S_a/S = i_c S_c/S,$$

where $S$ is the geometric surface area of the WE. In general, $S > S_a + S_c$, due to the presence of passive surface sites.

A working expression for the corrosion current ($i_{corr}$) can be obtained from Eq. 2 by setting the condition, $I_a = I_c = I_{corr}$, and by accordingly using $E = E_{corr}$ in the Butler Volmer expressions of $I_a(E)$ and $I_c(E)$. Simple calculations based on these considerations lead to the result:35

$$i_{corr} = \frac{i_{corr}}{S} = \frac{1}{S} \left( \frac{S_a}{S_c} \right)^{1/2} \left( \frac{S_c}{S_a} \right)^{1/2} \exp \left( \frac{SE^{0_a} - SE^{0_c}}{2RT} \right). \tag{3}$$

Where $i_{corr}$ is the corrosion current density, and $SE^{0_a} = E^{0_a} - E^{0_c}$. The exchange current densities, formal potentials (contained in the Nernst potentials) and Tafel factors are intrinsic parameters of the given mixed reaction. If these parameters are not significantly affected by surface modifiers, any passivation of the anodic and/or cathodic activities ( shrinkage of $S_a$ and/or $S_c$) would be directly manifested as a lowered value of $i_{corr}$. Likewise any cathodic and/or anodic boosts (expansion of $S_a$ and/or $S_c$) would result in an increased value of $i_{corr}$. By combining these observed trends of $i_{corr}$ with those of $E_{eq}$, it is possible to examine the mechanisms of CMP related surface modifications of metals.

The values of $E_{eq}$ and $E_{corr}$ for a given CMP system can differ from each other, because the adsorption characteristics of the slurry additives can be different in the two measurements. Specifically, in the measurement of $E_{corr}$, LSV is typically performed with positive voltage sweeps, which promotes the adsorption of anionic species during the entire scan. This in turn can result in a different value of $(S_c/S_a)$ compared to that expected during a simple potentiostatic hold at $E_{eq}$. The resulting value of $E_{corr}$ in this case would differ from its $E_{eq}$ counterpart.

In comparison with the case of $E_{corr}$, the surface conditions established during the measurement of $E_{eq}$ are closer to those of CMP. However, the $E_{eq}$ data do not generally indicate the mechanisms (enhancement or suppression of anodic/cathodic functions) responsible for shifting the values of $E_{eq}$ due to changes in the slurry compositions and/or mechanical effects. To detect these mechanisms, it is necessary to examine the actual current response of the metal-slurry interface. LSV measurements used to evaluate $E_{corr}$ readily provide this information (and also allow for a direct evaluation of $i_{corr}$, as long as the Tafel profiles of the polarization data are not distorted).
Potentiodynamic assessment of galvanic corrosion.— The galvanic current density \( i_\text{corr(A-C-A)} \) generated at the corroding anode (A) of a cathode-anode \( (\text{C-A}) \) couple can be determined by plotting together the polarization data for A and C.\(^6\) The cathode’s \( i_\text{corr} \) intersects the anode’s \( i_\text{corr} \) on such a plot, and the current coordinate of this intersection gives the net galvanic current \( i_\text{corr} \) of the given couple, where \( i_\text{corr(A)} = [i_\text{corr(A)} / S(A)] \) with \( S(A) \) denoting the anode’s surface area. To note the essential features of this current, we consider here a simple case where the active areas of the anode and cathode metals are equal. The considerations of Butler Volmer kinetics in this case lead to the following expression:\(^6\)

\[
i_\text{corr(A)} \approx \zeta_0 \cdot [\beta_\text{corr(A)} / \beta_\text{corr(C)}]^{1/2} \cdot \exp \left( \frac{\Delta E_\text{corr}}{2F} \right) \cdot \left[ \frac{1}{1 + \exp \left( \frac{\Delta E_\text{corr}}{2F} \right)} \right].
\]

where \( \beta(C) \approx \beta(A) \approx \beta \). The corrosion current densities of metals C and A, are denoted as \( i_\text{corr(C)} \) and \( i_\text{corr(A)} \), respectively. The corresponding corrosion potentials are \( E_{\text{corr}(A)} \) and \( E_{\text{corr}(C)} \), with \( \Delta E_{\text{corr}} = E_{\text{corr}(C)} - E_{\text{corr}(A)} \). The dimensionless parameter \( \zeta_0 \) represents a measure of the cathode’s current contribution to \( i_\text{corr} \).\(^6\) According to Eq. 4, minimizing galvanic corrosion basically corresponds to minimizing the value of \( \Delta E_{\text{corr}} \).

Considerations of tribo-electrochemical effects.— While Eqs. 1–4 assume a metal surface held in contact with a stationary electrolyte, using phenomenological considerations, the basic premise of these formulas can be extended to the polishing situation of CMP. The following effects of mechanical polishing are most relevant in the present context: (a) Convective transport of reactants to the metal surface, (b) mechanical removal of chemisorbed but un-complexed additives from the metal and metal oxide sites, and (c) mechanical removal of complexed species to recover bare metal sites. Effect (a) boosts the local concentration of reactants, and therefore, increases removal of complexed species to recover bare metal sites. Effect (b) and (c) alter the values of \( S_1 \) and \( S_2 \) with respect to those of an un-polished surface, and accordingly affect the measured parameters, \( E_{\text{corr}}(I_\text{corr} / S) \) and \( (I_\text{corr}/S) \).

The removal of chemically formed surface complex films in CMP usually requires the joint action of a polishing pad and abrasive particles, while polishing at a low pressure with the pad alone may not be adequate to complete the task. If the sample surface in such a case is polished by a pad in an abrasive free solution, only the aforementioned effects (a) and (b) will likely be measurable. Full manifestation of all three effects (a)-(c) in the polishing stage will be expected while using abrasive-added slurries. The relative roles of these effects in the surface chemistries of such CMP systems can be checked by carrying out the following four sets of comparative measurements: Polishing of the WE (i) with and (ii) without abrasive particles; and holding (iii) with and (iv) without abrasive particles.

Experimental

The experimental setup assembled for tribo-electrochemical measurements was similar to those reported previously.\(^38,39\) In brief, the three-electrode test cell had two separate parts. The lower part of the cell was a beaker-like cylindrical container made of Teflon, fixed to the rotating platen of a Struers Benchtop polisher. An IC1000 polishing pad, cut in a circular shape to fit the cell-diameter was attached to the cell’s floor. The metal test sample (1.25, 0.5”, and 1.17” diameter, 0.125” thick disc of 99.95% pure Cu, Ru, and Ta), entrenched in a Teflon holder with only a flat circular surface exposed, was attached to the rotating polishing head; this constituted the upper part of the tribo-electrochemical cell. For all experiments, the sample surface was pressed down onto the pad at a pressure setting of 2 psi. The experimental cell was controlled by a PAR VersaStat4 potentiostat.

The alkaline slurry solution of 25 mM SPC + 0.5 wt% GC was prepared using reagent grade chemicals (Sigma Aldrich) and triply distilled water. Polarization measurements were performed using LSV at a scan rate of 5 mV s\(^{-1}\) both with and without the inclusion of 5 wt% colloidal silica (NexSil 12). During stationary hold stages, the concentration of these particles at the sample surface was prone to variations due to adsorption and diffusion motion. By considering that such variations in the WE surface conditions could potentially be unsuitable for steady state EIS,\(^7\) impedance spectra were only recorded in abrasive free solutions. The pH values of the solutions (10.74 and 10.31, without and with 5 wt% SiO\(_2\), respectively) did not show any significant changes after the LSV treatments.

A saturated calomel electrode (SCE) reference, held in a fixed glass chamber was connected to the rotating cell compartment using a salt bridge. The counter electrode consisted of a stainless steel plate electrically connected to a Cu ring fixed to the outside wall of the cell. Two carbon brushes pressed against the Cu ring were used to electrically access the counter electrode. A similar arrangement was used to connect the WE to the potentiostat. Tribological conditions were established by polishing the WE during electrochemical measurements. Both the platen (pad) and the head (WE holder) of the polisher were rotated at an angular velocity of 90 rpm. The relatively thick polycrystalline disc electrodes were not suitable for accurate evaluation of removal rates, and hence such measurements were not attempted in this work. The polish runs were carried out to record the effects of abrasion on the electrochemical data, but not to determine removal rates.

The OCP as well as the polarization data were collected alternately between repeated polishing and non-polishing hold cycles, spending 4 min in each cycle. Both the polisher head and the platen were kept stationary during the hold cycles, but the sample always remained pressed against the pad at the same applied pressure (2 psi). EIS was only performed during the hold periods, and using A.C. perturbation voltages of 5 mV average amplitude in the frequency range between 1 Hz and 10 kHz with 190 frequencies. The electrode was allowed to stabilize at the OCP before each round of EIS runs, and multiple spectra were recorded for comparisons at each setting to ensure the absence of transient changes during data collection. The EIS data, processed as Nyquist impedance plots, were validated by input-vs.-output frequency comparison,\(^40\) and were fitted to EEC models developed by complex nonlinear least square (CNLS) calculations using ZSimpWin.

Results and Discussion

Open circuit potential and potentiodynamic polarization data recorded with and without surface polishing in an abrasive-free slurry solution.— Fig. 1 shows OCP transients measured for (A) Cu, (B) Ru and (C) Ta discs in the abrasive free solution of 25 mM SPC + 0.5 wt% GC. In each case, the metal surface is repeatedly cycled through a polishing stage, followed by a hold period. These data are associated with some voltage noises due to recurrent formation and elimination of corrosion sites, and the noises increase during the polishing stages.\(^41\) Tribological measurements of OCP transients have been previously reported for Ta.\(^2,21\) Cu\(^{11-13}\) and Ru.\(^4\) For some of the slurry compositions used in these earlier studies, the OCPs of all three metals have shown a decreasing trend while polishing, and a reversed trend emerged in the holding stages. These effects have often been attributed to the removal and subsequent regeneration of anodically passivating surface films in the polish and hold stages, respectively. Lee and Park have reported a different behavior of \( E_{\text{oc}} \) in the CMP of Ru, where the value of \( E_{\text{oc}} \) increased during surface abrasion;\(^14\) this trend has also been observed in Shima et al.’s investigation of Cu CMP.\(^13\) The present results in Fig. 1 are in the latter category. Table I includes the changes (\( \delta E_{\text{oc}} \)) in the OCP values detected in the transition from the polishing to the hold stages; \( \delta E_{\text{oc}} = E_{\text{oc}}(\text{polish}) - E_{\text{oc}}(\text{hold}) \).

The \( E_{\text{oc}} \) values observed in Fig. 1, in combination with the known solution pH (~10) serve to locate the experimental metal-solution systems on their respective Pourbaix diagrams.\(^25,26,28\) This helps to categorize the expected oxide/hydroxide compounds of Cu, Ru and Ta in the abrasive-free alkaline base used here. By combining this information with previously published results for similar systems,\(^4,15-17,45\) we compile in Table I the predominant electrode species expected under the experimental conditions of Fig. 1. The SPC dissolved in the
Figure 1. OCP transients measured for (A) Cu, (B) Ru, and (C) Ta discs during alternately sequenced 4-min segments of polishing and stationary hold in an abrasive free solution of 25 mM SPC + 0.5 wt% GC at pH = 10.74. The polishing was performed with both the platen and the disc rotated at a speed of 90 rpm, and the metal disc was kept against the polishing pad at a down-pressure of 2 psi during both the polishing and the hold cycles.

Table I. Surface species and polish-induced equilibrium potential shifts of Cu, Ru and Ta electrodes.

|                |Cu | Ru | Ta        |
|----------------|----|----|-----------|
|Surface species |Cu2O, CuO, Cu2O3(OH)2, [CuCO3(OH)2]2−, Ru, Ru(OH)x, RuO2, RuO2−2, Ru-Gnd complex, Ta2O5, Ta2.nH2O, Ta-Gnd complex |Cu, Cu2O, CuO, Cu2CO3(OH)2, [CuCO3(OH)2]2− |Ru, Ru(OH)x, RuO2, RuO2−2, Ru-Gnd complex |
|δEoc in abrasive free solution (mV)a |6.7 |27.8 |8.8 |
|δEcorr in abrasive free solution (mV)a |189.8 |52.1 |Not measurable due to current noise |
|δEoc in abrasive added slurry (mV)a |4.3 |35.4 |−403.4 |
|δEcorr in abrasive added solution (mV)a |35.0 |102.7 |−604.8 |

Figure 2. Potentiodynamic polarization plots for (A) Cu, (B) Ru, and (C) Ta discs recorded at a voltage scan rate of 5 mV s−1 while the metal surface was (a) polished or (b) held stationary in an abrasive free solution of 25 mM SPC + 0.5 wt% GC at pH = 10.74. The polishing conditions were the same as those used in Fig. 1.

slurry releases H2O2 and CO32− and at the solution pH used, a major fraction of the CO32− converts to HCO3−.46 The guanidinium cation, Gnd+ (CH6N3+ pKa = 13.6) released by GC acts as an additional complexing agent. The surface species listed in Table I result mostly from metal specific anodic or nonfaradaic chemical reactions of the slurry additives. These reactions are supported by the cathodic steps of H2O2 reduction as well as the oxygen reduction reaction (ORR).15,47 The OCP-changes accompanying the application/withdrawal of surface abrasion in Fig. 1 can be associated with correspondingly activated selective changes in the values of Sα and/or Sc in Eq. 1. Since the ORR in alkaline media produces OH−,48,49 the cathodic sites of O2 reduction tend to be mutually exclusive with respect to the anodic sites of OH− adsorption. The cathodic ORR usually favors terrace sites of the WE,50 while the anodic reactions of hydroxide/oxide formation are promoted at the adatom sites.51 Likewise, on oxide coated electrodes, the ORR mostly occurs through porous regions of the oxide layer.22 On conductive oxides (like RuO2), the ORR is favored on the sites that can accommodate side-on adsorption of O2 to allow an O-O bridge formation.52

Fig. 2 shows LSV-measured potentiodynamic polarization plots for (A) Cu, (B) Ru and (C) Ta discs, (a) with and (b) without polishing the sample surfaces in the abrasive-free SPC-GC solution. These plots exhibit the signature current noises of tribo-corrosion due to repeated activation and passivation of distributed reaction sites.53 The noises are absent under the hold conditions, where the surface adsorbate coverages only respond to voltage variations. The detailed features of current noises for tribo-corrosion usually are different from those of the corresponding voltage noises.34,55 This is seen in Fig. 2, where the
noise amplitudes are more system-specific compared to the case of Fig. 1. While the current noises for Cu and Ru are mutually comparable, the valve metal Ta shows much stronger noise signals due to its high efficiency for regenerating surface oxides.36,57

The cathodic and anodic current branches of each polarization plot in Fig. 2 meet at $E_{\text{corr}}$. As expected in view of Eq. 1, $E_{\text{corr}}$ exhibits the same polish-vs.-hold trends as those observed for $E_{\text{oC}}$ in Fig. 1. The polish induced increments [δ$E_{\text{corr}}$ = $E_{\text{corr}}$ (polish) – $E_{\text{corr}}$ (hold)] of $E_{\text{corr}}$ are compiled in Table I; this error is omitted for the Ta data in Fig. 2C, where strong current noise makes it difficult to accurately determine $E_{\text{corr}}$. The system specific parameters $E_{\text{corr}}$ and δ$E_{\text{corr}}$ are different from their corresponding open circuit values, $E_{\text{oC}}$ and δ$E_{\text{oC}}$.

As we noted earlier, these differences can be attributed to the different chemisorption characteristics acquired by the metals between the OCP and the LSV experiments.

In Fig. 2A, both the cathodic and the anodic current branches of plot (a) are shifted toward higher values compared to those of plot (b). However, the overall increase in the cathodic current is stronger than the corresponding increase in the anodic branch. This is particularly notable if the currents from plots (a) and (b) are compared in the low overpotential region, and the results for (a) are indicative of a preferential increase in the value of $S_c$ compared to that of $S_a$. According to Eq. 1, this places $E_{\text{corr}}$ (Cu-polish) above $E_{\text{corr}}$ (Cu-hold), and the corresponding $E_{\text{oC}}$ data also follow the same trend.

Like the case of Cu, the plots for Ru in Fig. 2B indicate an abrasion induced selective rise in the cathodic polarization, and hence a corresponding upward placement of $E_{\text{corr}}$ (Ru-polish) compared to $E_{\text{corr}}$ (Ru-hold). This trend is also shared by the $E_{\text{oC}}$ data for Ru in Fig. 1B. For Ta in Fig. 2C, abrasive free polishing of the surface preferentially moves the anodic current branch to lower currents. This effect is responsible for increasing $E_{\text{corr}}$ (Ta) during the polishing stage in Fig. 1C. A similar behavior is also expected for $E_{\text{corr}}$ (Ta), although this effect is mostly obscured by the current noise in Fig. 2C(a).

Open circuit potential and potentiodynamic polarization data recorded with and without surface polishing using abrasive based slurry of colloidal SiO$_2$.— Fig. 3 shows OCP transients for (A) Cu, (B) Ru and (C) Ta discs, recorded using 25 mM SPC + 0.5 wt% GC + 5 wt% colloidal SiO$_2$ and applying sequentially alternating cycles of polish and hold. As is the case in Fig. 1, the OCPs of Cu and Ru increase during polishing and drop during the stationary hold. For Ta, however, this trend is now reversed, and the plots resemble those previously reported for Ta using other abrasive slurries.12,13 The abrasion induced OCP shifts, δ$E_{\text{oC}}$, measured from Fig. 3 are included in Table I. These δ$E_{\text{oC}}$ values are larger than those measured for the SiO$_2$ free solution, because the process of surface-film removal becomes more efficient when polishing is done with abrasive particles. In addition, SiO$_2$ particles contain SiOH groups that form bonds via chemical interactions with the surface being polished.58 These abrasive–surface interactions also contribute to the detailed data features seen in Fig. 3.

Figs. 4A, 4B and 4C shows potentiodynamic polarization plots for the systems considered in Figs. 3A, 3B and 3C, respectively. The $E_{\text{corr}}$ data in Fig. 4 follow the same polish vs. hold patterns displayed by their $E_{\text{oC}}$ counterparts in Fig. 3. The δ$E_{\text{corr}}$ values for Cu and Ru taken from Fig. 4 (and included in Table I) are somewhat different from those measured in the SiO$_2$ free solution. These differences can be attributed to the aforementioned interactions of SiO$_2$ particles. Nevertheless the different behaviors of Ta found between Figs. 1C (2C) and 3C (4C) are considerably more pronounced than those expected only from chemical interactions of abrasives, and therefore, could be associated with the main effect of surface abrasion, namely material removal.

A comparison of plots (a) and (b) in Fig. 4A shows a moderate yet preferential cathodic increment in the faradic activity of Cu resulting from the polishing action of SiO$_2$. This leads to a positive value of δ$E_{\text{corr}}$ (as well as of δ$E_{\text{oC}}$). In Figs. 4B, polishing increases both the anodic and the cathodic currents of Ru, but the increase is favorably stronger on the cathodic side. As a result, once again we measure δ$E_{\text{corr}}$ > 0 (and δ$E_{\text{oC}}$ > 0) in this case. In Fig. 4C, the abrasive based polishing only weakly affects the magnitude of the cathodic current of Ta, while the corresponding anodic current undergoes a substantial increase. This anodic preferment of Ta is responsible for the negative values of δ$E_{\text{corr}}$ and δ$E_{\text{oC}}$ resulting from Figs. 4C and 3C, respectively. The reaction mechanisms of the aforementioned effects are examined next.

CMP-specific surface modifying reactions of Cu, Ru and Ta.— The H$_2$O$_2$ supplied by SPC in the slurry solution breaks down in a reduction step,57

$$\text{H}_2\text{O}_2 + 2e^- = 2\text{OH}^-,$$

and this reaction contributes to the cathodic component of the mixed potential activities of all three metals. The ORR,59

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- = 4\text{OH}^-,$$

represents the other cathodic feature shared here by the three metals. LSV activated currents of reactions [5] and [6] contribute to the cathodic branches of the polarization plots in Figs. 2 and 4. The standard potentials of both reactions [5] and [6] (0.637 and 1.6 V, respectively) are higher than those of the typical anodic steps responsible for generating the hydroxides and oxides of Cu, Ru and Ta.49 This forms the basis for the mixed potential systems used here.

The anodic reactions of Cu in the alkaline SPC-GC solution include:

$$2\text{Cu} + 2\text{OH}^- = \text{Cu}_2\text{O} + \text{H}_2\text{O} + 2e^-,$$

$$\text{Cu} + 2\text{H}^- = \text{Cu} + \text{H}_2 + 2e^-,$$

$$\text{Cu}_2\text{O} + \text{HCO}_3^- + \text{OH}^- = 2\text{Cu} + \text{CO}_3\text{(OH)}_2 + 2e^-.$$

Figure 3. Open circuit potential transients measured for (A) Cu, (B) Ru, and (C) Ta discs during alternately sequenced 4-min segments of polishing and stationary hold in a CMP slurry of 25 mM SPC + 0.5 wt% GC + 5 wt% colloidal SiO$_2$ at $pH$ = 10.31. All other experimental conditions were the same as those used for Fig. 1.
where Cu₂CO₃(OH)₂ as well as the Cu-oxides are surface passivating species. The passivation feature of Cu observed around 0 V in Fig. 2A(b) can be linked to Cu₂CO₃(OH)₂ surface films formed due to anodic activation. Surface polishing by the pad alone is sufficient to remove this species, and hence the anodic passivation is absent in Fig. 2A(a). A weak cathodic passivation structure is observed in Fig. 2A(a) due to rapid depletion of the interfacial [O₂] and [H₂O₂] at the high negative overpotential.

The mixed potential combination of reactions [6] and [7] has the form: 2Cu + (1/2) O₂ = Cu₂O, while reactions [5] and [8] combine as: Cu + H₂O₂ = CuO + H₂O. The Gnd⁺ released from GC frequently plays an active role in supporting the surface complexes for metal CMP. In the case of Cu, the formation of such complexes most likely relies on a synergistic action of other additives, so that the efficiency of the process is dictated by the detailed slurry composition. Depending on the overall slurry formulation in this case, the complexing function of Gnd⁺ may or may not be readily observable in the case of Cu CMP. A situation of the latter kind can be noted in the results of Li et al., where the removal rate of Cu remained largely invariant with respect to variations of [Gnd⁺] (0.2 to 1.0 wt%) in an alkaline medium.59 The slurry composition used in the present work also seems to be in this category, since no clear signatures of Cu-Gnd complex formation are detected in the electrochemical data discussed here.

In alkaline solutions, the reduction of H₂O₂ on Cu tends to rely on a catalytic mechanism involving Cu₂O-CuO binary surface films.60 This requires the presence of adsorbate-free and un-complexed Cu-oxides on the Cu-WE surface. It has also been suggested that, the alkaline ORR at the oxide sites of a metal (M) occurs through an outer sphere charge transfer mechanism by electron tunneling to hydrated oxygen species of the form O₂(H₂O)₆.61 This reaction takes place at the M-OH sites of the metal oxide, and is mostly constrained if these sites are complexed and/or covered by other chemisorbed additives (such as Gnd⁺ and/or HCO₃⁻). This shielding of Cu-oxide sites from H₂O₂ and O₂ is likely responsible for the relatively lessened cathodic activity of Cu in Fig. 2A(b).

If abrasive-free polishing is applied, the un-complexed adsorbates are removed from the electrode’s Cu-oxide regions, while the already complexed oxides can still remain mostly intact. This opens up the additive covered M-OH sites needed for the reduction steps [5] and [6], and consequently the cathodic function of the electrode surface increases. In addition, the rotating sample/pad system promotes convective transport of solvated O₂ to the electrode surface, which increases Iₒ, and further promotes the electrode’s cathodic activity. These effects can be associated with the cathodic upturn of plot (a) in Fig. 2A.

If the Cu surface is polished using the SiO₂ based slurry, the complexed and un-complexed oxide sites of Cu are effectuallly removed. Both the anodic and cathodic activities of the electrode increase in this case, but the cathodic branch becomes comparatively stronger. This suggests that, the steady state surface density of the cathodic sites (un-complexed oxides) maintained during SiO₂ supported polishing most likely is higher than that of the anodic sites (bare metal, regenerated by complex removal).

The anodic steps favored at the Ru surface in Fig. 1B are:

\[
2Ru + 3OH⁻ \rightarrow Ru(OH)₃ + 3e⁻, \quad [10]
\]

\[
Ru(OH)₃ + OH⁻ \rightarrow RuO₂ + 2H₂O + e⁻, \quad [11]
\]

and the net reaction of Eqs. 5 + 10 + 11 has the form: Ru + 2H₂O₂ = RuO₂ + 2H₂O. The Ru surface in the present experiments should be mostly covered by this RuO₂. In view of previously published results,52 the cathodic function of this oxide for supporting the reduction of H₂O₂ and O₂ should also be affected by ion adsorptions. These adsorption mediated effects would depend on the ion-surface electrostatic interactions (a critical factor of site specific reactions) governed by the effective surface charge of the metal. Due to its electrically conductive nature, RuO₂ constitutes an amphifunctional surface where both its potential of zero charge (PZC) and its isoelectric point (IEP) control the surface charge.62

The PZC of RuO₂ in aqueous solutions resides between −0.2 and 0.0 V,63 and this range is below the typical Econt values of Ru found in Figs. 2 and 4. The IEP of RuO₂ is 5.3,64 which falls below the solution pH used here. The Gnd⁺ cation can effectively chemisorb onto the negatively charged sites of bare Ru, as well as RuO₂; this would facilitate the generation of mechanically removable surface films of Ru-Gnd complexes.4 While the same time, HCO₃⁻/CO₃²⁻ can chemisorb onto some of the RuO₂ sites to form anion incorporated structurally weak island films.35 In addition, reactions [5] and [6] can increase the local pH at the electrode surface, and thus can further destabilize/weaken the RuO₂ films by the dissolution reaction: RuO₂ + 4OH⁻ = RuO₂²⁻ + 2H₂O + 2e⁻. The coupled form of this step with the ORR is: RuO₂ + 3OH⁻ + (1/2) O₂ = RuO₂²⁻ + H₂O.

While the Ru-Gnd complex films, and the anion incorporated oxides serve as chemically removable surface materials, if not polished off the Ru surface, they can lower the metal’s faradaic activity. The polishing pad’s abrasion without SiO₂ can remove superficially adsorbed HCO₃⁻/CO₃²⁻ from RuO₂ to renew the cathodic actions of H₂O₂ and O₂ (case of Figs. 1B and 2B). Abrasion in the presence of SiO₂ particles further enhances this effect along with some regeneration of the electrode’s anodic function through the removal of Ru-Gnd complex films (case of Fig. 3B and 4B).

The mixed potential reactions of Ta include reactions [5] and [6] on the cathodic side, and the anodic steps:53,56 Ta₂O₅ + 10H⁺ = Ta₂O₅ + 5H₂O + 10e⁻. The combined steps of this reaction with Eqs. 5 and 6 have the forms: 2Ta + 5H₂O₂ = Ta₂O₅ + 5H₂O and 2Ta + (5/2)O₂ = Ta₂O₅, respectively. The Ta electrode surface is effectively covered by this Ta₂O₅ product. In the alkaline environment used here the Ta-oxide
Surface is heavily populated by Ta-O\(^-\) groups. Through electrostatic interactions, these species can provide a favorable substrate for Gnd\(^+\) adsorption, which is necessary to form mechanically removable Ta-Gnd surface complexes.\(^{67}\) The Ta-oxide/Ta-Gnd surface film tends to be porous due to the formations of metatantalate (Ta\(_2\)O\(_x\) + 2OH\(^-\) = 2TaO\(_3\) + H\(_2\)O) and unstable tetraperoxo complexes, [Ta(O\(_2\))\(_4\)]\(^3+\), within the film.\(^{68}\) Transport of reactants through these pores to the underlying Ta is responsible for sustaining the faradic activity of Ta in Fig. 2C(b).

Abrasive free polishing with the pad inefficiently/partially disintegrates the surface film, and this also generates localized debris. detachment and random reinsertion of the insoluble debris occurring at the surface film of Ta promote the oscillatory feature of localized activation and re-passivation.\(^{69}\) The strong current noise observed in Fig. 2C(a) is likely caused by this process. The interfacial accumulation of insoluble fragments during abrasive free polishing also introduces some anodic surface passivation of Ta in Fig. 2C(a). This anodic passivation is manifested in Fig. 1C by increasing \(E_{oc}\) (Ta) in the abrasive free polishing cycles.

In the SiO\(_2\) added system, the polishing is considerably more effective in removing the surface film, and hence the localized activation-passivation in this situation is suppressed together with its consequential current noise. In addition, the effects of locally accumulated debris on the electrode current are mostly eliminated as the SiO\(_2\) particles carry away the polished fragments from the pad-sample interface.\(^{70}\) It is the case of Fig. 4C(a). Since the surface films of Ta are more effective in blocking anodic reactions than cathodic reactions,\(^{71}\) the effective removal of these films by SiO\(_2\) selectively increases the anodic electrode current in Fig. 4C. This abrasive supported effect of anodic augmentation is also displayed in Fig. 3C, where \(E_{oc}\) (Ta) decreases during polishing in the SiO\(_2\) added slurry.

Controlling galvanic corrosion.—The three metals examined here represent two different galvanic couples, Ru-Cu and Cu-Ta, which are likely to form in the CMP steps for Ru and Ta, respectively. The corrosion parameters that determine \(i_g\) according to Eq. 4 for these C-A type bimetallic couples are collected in Figs. 5 and 6 from the results of Figs. 1–4. The \(i_{corr}\) and \(i_{corr}\) values for Ta in polish without SiO\(_2\) could not be determined reliably due to the current noises in Fig. 2C(a). In additive free aqueous media, Cu and Ta serve as the anodes of the Ru-Cu and Cu-Ta galvanic couples, respectively. An inspection of the equilibrium potentials in Fig. 5 indicates that the presently used slurry solutions maintain this noble-active order of the Cu-Ta couple. However, a weak reversal of the galvanic polarity is observed for some of the Ru-Cu systems where Ta.\(^{72}\) Presently used slurry solutions maintain this noble-active order of the Ru-Cu couple. However, a weak reversal of the galvanic polarity is observed for some of the Ru-Cu systems where \(E_{corr}\) is close to zero but negative. The \(i_{corr}\) values in Fig. 6 are comparable to those previously found in other CMP studies of Ru.\(^{73}\) Ru and Ta.\(^{74}\) In Fig. 6, \(i_{corr}\) (Cu) increases in going from the hold to polishing stages, both with and without the inclusion of SiO\(_2\). This is consistent with the corresponding faradaic boost of polishing observed in Figs. 2 and 4. The values of \(i_{corr}\) (Ru) are comparable between the hold and polish cycles in the SiO\(_2\) free system, which is also seen in the mutually close placements of plots (a) and (b) in Fig. 2B. In the SiO\(_2\) added slurry, \(i_{corr}\) (Ru) increases in agreement with the congruently increased cathodic activity of Ru manifested in Fig. 4B(a). Likewise, the increased anodic action of Ta during abrasive supported polishing increases the accompanying value of \(i_{corr}\) (Ta).

To determine \(i_g\) by the method of intersecting polarization plots,\(^{63}\) in Fig. 7 we have grouped these plots for the three metals based on their measurement conditions. A number of these systems exhibit rather low driving potentials \(\Delta E_{corr}\) for galvanic corrosion (which is also seen in Fig. 5), and hence do not support any measurable galvanic currents. These include: Cu-Ta in hold with (Fig. 7C) and without (Fig. 7A) SiO\(_2\); Ru-Cu in polish without SiO\(_2\) (Fig. 7B) and in polish with SiO\(_2\) (Fig. 7D). For the Cu-Ta system in polish without SiO\(_2\), no reliable values of \(i_g\) could be obtained due to the strong current noise of Ta in this case (Fig. 7A). Measurable values of \(i_g\) were only detected for three of the galvanic systems examined, and these currents are noted in Figs. 7A, 7C and 7D.

The results of Fig. 7 indicate that, the galvanic corrosion characteristics of a given bimetallic system for CMP may vary between polishing and stationary settings. However, this distinction is likely
to be system specific, because the results of $i_g$ measurement can be affected by wear-corrosion synergisms, which would depend on the metal and the chemical environment of CMP. Therefore, $i_g$ should ideally be determined, whenever possible, under tribological conditions close to those of actual CMP. The results obtained here in the latter approach show that, $i_g$ (Ru) in the Cu-Ru couple (Fig. 7C) is lower than the general $i_{corr}$ values of the individual metals (Fig. 6). Thus the slurry formulation explored here is effective in minimizing galvanic corrosion effects in the CMP of Ru and residual Cu. However, the value of $i_g$ (Ta) in Fig. 7C is larger than $i_{corr}$ (Ta) found under the same experimental conditions in Fig. 6. This demonstrates that the formulation of a given barrier-CMP slurry may require further compositional adjustments when the barrier material is changed.

**Results of impedance spectroscopy.**—EIS was used as an additional check of the reaction schemes described in Eqs. 5–11. Nyquist impedance spectra for the Cu, Ru and Ta samples were collected in the abrasive free SPC-GC slurry, and by applying stationary hold conditions at the respective OCPs of these systems. The symbols in Fig. 8 show the Nyquist data for (A) Cu, (B) Ru and (C) Ta, while the lines represent CNLS fits using the common EEC shown in Fig. 9A. The insets show close-up views of the detailed high-frequency structures in the Nyquist plots.

$C_a$ denote the solution resistance and the metal’s effective double layer capacitance, respectively; the other elements are linked to the CMP specific reaction steps. The reactions considered here for the three metals share a common pattern, namely in all three cases the initial step is the surface adsorption of reactants. These adsorption steps have been modeled in terms of the constant phase element (CPE) $Q_a$, connected in parallel with an
adsorption resistance $R_a$. The post-adsorption oxidation and reduction steps have been modeled with the resistances $R_{1u}$ and $R_{1z}$, respectively. The resistance $R_a$ accounts for any additional faradaic steps supported by the oxide/hydroxide surface sites (e.g., Eqs. 9 and 11). Thus in the effective EEC of Fig. 9A, $R_a = R_a + (1/\omega R_a) + (1/R_{1z})^{-1}$.

In the EIS experiments of Fig. 8, the transport of reactants to the WE occurred via diffusion through the limited space available at the pad-metal interface. To account for this effect, a Nernst diffusion element ($Z_d$), connected in series with $R_a$, was initially introduced in the reaction branch of the trial circuit. Following previously published guidelines, this $Z_d$ was taken as a finite length Warburg element with a transmitting boundary at the WE surface. However, it was found in repeated trials of CNLS calculations that, a diffusion element was unnecessary to fit the data. Forced inclusion of $Z_d$ in the EEC yielded large errors in the calculated elements. This indicated that the impedance contribution of diffusion was minor compared to the net impedance of the other elements in the reaction branch of Fig. 9B. To further examine the implications of these observations, we compared the following two competing length scales associated with the transport of reactants: The characteristic diffusion length ($L_d$) sensed by EIS, and the minimum distance ($L_m$) available for free diffusion at the pad-WE interface. From phenomenological considerations one might expect that, depending on the experimental system, the diffusion signatures of $Z_d$ would remain undetected if $L_d < L_m$.

$L_d$ is on the order of $(D/\omega)^{1/2}$, where $D$ and $\omega$ denote the diffusion coefficient of the reactant species and the perturbation frequency of EIS, respectively. Using $D \sim 10^{-5}$ cm$^2$ s$^{-1}$, this estimate for $L_d$ varies between 0.13 and 13 $\mu$m within the spectral range of EIS explored here. For the stationary sample configuration of EIS, the solution species stored within the pores of the polishing pad likely serve as the main source of reactants. Hence, an appropriate estimate for $L_m$ is the typical diameter of these pores, which varies in the 30–70 $\mu$m range. Based on these estimates, $L_d$ is indeed less than $L_m$ for the present EIS measurements, which explains the absence of a diffusion element in the EEC resulting from these experiments.

The final CNLS-analyzed EEC of Fig. 9A yielded satisfactorily fits to all the impedance spectra recorded here with $<5\%$ uncertainties in each constituent element of the model. The impedance parameters obtained from these fits are listed in Table II. The double layer capacitances of adsorbate free metal electrodes in aqueous electrolytes at room temperature typically vary in the 20–50 $\mu$F cm$^{-2}$ range. In Table II, only $C_{dl}$(Cu) falls in this range, while $C_{dl}$(Ru) and $C_{dl}$(Ta) have notably lower values. As elucidated below, this is a consequence of partial surface passivation due to oxide species formed on the electrodes in the stationary sample settings of EIS.

### Table II. Impedance parameters of Cu, Ru and Ta electrodes in abrasive free alkaline solution of 25 mM SPC and 5 wt% GC.

|   | Cu   | Ru   | Ta   |
|---|------|------|------|
| $R_a$ ($\Omega$ cm$^2$) | 509.8 | 153.5 | 423.7 |
| $C_{dl}$ ($\mu$F cm$^2$) | 1.65  | 38.5  | 3.01  |
| $R_{1u}$ ($\Omega$ cm$^2$) | 60.2  | 10.7  | 127.1 |
| $Q_{dl}$ ($\mu$F cm$^{-2}$ s$^{1/2}$) | 41.4  | 276.0 | 21.0  |
| $n$ | 0.75  | 0.77  | 0.83  |
| $R_{1z}$ (kΩ cm$^2$) | 16    | 0.18  | Infinite (open branch) |
| $\tau_r$ (ms) | 0.33  | 0.50  | 0.79  |

Since the double layer capacitances are not detected here as frequency dispersed CPEs, any oxide layers contributing to the effective values of $C_{dl}$ should be spatially homogeneous. A porous surface oxide layer of this type can be modeled as a parallel plate capacitor, $C_{ox}$, connected in series with $C_{dl}$, the double layer capacitance for the bare metal. The resulting net capacitance of the combination is:

$$C_{ox} = (1/\omega R_{1z})^{-1}$$

The metal dependent trends observed in the values of $R_a$ and $C_{dl}$ in Table II are mutually opposite, because the measured value of $R_a$ contains a series connected resistive component of the oxide surface film. This $R_a$ also includes a series contribution of the solution confined in the salt-bridge tube used.

The frequency dispersed CPE behavior of the capacitive adsorption element is indicative of inhomogeneous adsorption sites for the reactants. This is in agreement with the preferential adsorption characteristics of different solution species, as expected in view of the anodic-cathodic selectivity of CMP reactions discussed earlier in this report. $T_0$ and $n$ ($0 \leq n \leq 1$) are CPE parameters that define the impedance of the $Q_{dl}$ as $K(\omega)^n$, where $\omega$ is the perturbation frequency of EIS. The relaxation time ($\tau_r$) for the faradaic adsorption step dictates the overall surface activity (reaction rates) of the test metal, and can be evaluated as:

$$\tau_r = (V_0(1/R_a) + (1/R_{1z})^{-1})^{-1/n}$$

The resulting values of $\tau_r$ are included in Table II, and are comparable to those reported for anion adsorption reactions on metal electrodes; this provides further support to the proposal that the surface modifying reactions studied here are dominated by anodic steps of adsorbed anions. In Table II, the metal specific faradaic conductance ($1/R_{1z}$) is used to decrease in the order $\text{Ru} > \text{Cu} > \text{Ta}$, and this same order is also observed in the values of $\epsilon_{\text{cap}}$ in Fig. 6. Thus the findings of the A.C. and D.C. measurements fully agree with each other.

### Conclusions

The present study explores a tribo-electrochemical protocol for characterizing metal CMP systems by combining strategic measurements of mechanically affected OCP and LSV with steady state EIS. The alkaline slurry composition used in these experiments is designed to support low-pressure CMP of Ru, Ta and residual Cu, with a specific focus on the reduction of galvanic corrosion effects. The LSV-measured corrosion parameters indicate that the proposed slurry formulation is effective in mitigating these galvanic effects in the Ru-Cu system, both under non-polishing and polishing (with or without SiO$_2$ abrasives) conditions. For the Ta-Cu system, galvanic corrosion of Ta is suppressed in the absence of polishing as well as in the presence of polishing without abrasive particles, because the protective surface layers of Ta-oxide-complexes partially remain intact in these cases.
Polishing with SiO₂ particles effectively removes these layers, and then the Ta surface becomes prone to galvanic corrosion as an anode of the Cu-Ta couple. Further adjustment of the slurry composition using a corrosion inhibitor may be necessary in the latter case.

The OCP of the metal-slurry interface is quite sensitive to the application/withdrawal of mechanical abrasion, and hence can serve as an effective probe of the interacting chemical and mechanical roles of CMP. However, the underlying mechanisms of such tribo-electrochemical signals are found to be system-specific, and are largely governed by the intrinsic surface passivation characteristics of the given metals. Identifying the mechanistic details of these effects is critical to the advancement of slurry engineering for metal CMP. The tribo-electrochemical experiments reported here in combination with stationary state EIS demonstrate the utility of such measurements in this regard.

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