The Utility of Zeta Potential Measurements in the Characterization of CMP Slurries

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Dispersed Systems

An **interface** always exists when one component (phase I) is dispersed in a state of subdivision in a medium (phase II)

Two *fundamental* parameters control the nature and behavior all dispersed systems

- **Extent of Interface**
- **Interfacial Chemistry**
- **Stability and Structure**
- **System Properties**

The interfacial extent and interfacial chemistry are not independent parameters.
Measurement Techniques used to Characterize Particulate Suspensions

INTERFACIAL EXTENT ↔ INTERFACIAL CHEMISTRY

Particle Size and Distribution*
Particle Shape and Morphology*
Surface Area* (external/internal)
Porosity

Surface Charge*
Nature/type of group(s)
Number and distribution
Dissociation/ionization
Preferential adsorption
Hydrophobic/hydrophilic balance
Surface (interfacial) Tension
Contact Angle

*
The Nature of Surface Charge in Water

Mineral oxide crystal lattices are anisotropic
- charge development because of \( n \) and \( p \) defects in crystal structure
- results in hydroxyl groups (-OH) \( \ddagger \) can undergo reaction with either H\(^+\) or OH\(^-\)
- difficult to control surface chemistry in manufacture and processing
  - reactant impurities

Metal Oxide Surfaces in Water
Adsorption of protons and hydroxyl ions
\[
H^+ \leftrightarrow OH^- \\
MOH_2^+ \Leftrightarrow MOH \Leftrightarrow MO^- + H_2O
\]

Formation of hydroxylated species
\[
M^{n+} + xOH^- \Leftrightarrow M(OH)_{x}^{(n-x)^+} \\
M(OH)_{x}^{(n-x)^+} + OH^- \Leftrightarrow M(OH)_{x+1}^{(n-x-1)^+} \\
M(OH)_{x+1}^{(n-x-1)^+} + H^+ \Leftrightarrow M(OH)_{x-1}^{(n-x+1)^+}
\]

Dissociation driven by pH
\( \ddagger \) avoid swings in pH

Equilibria driven by particle concentration
\( \ddagger \) constant %solids
Nanoparticle Surface Chemistry

10nm particle size:  
ca 30% of molecules/atoms that comprise the molecular structure become “surface moieties”

1nm particle size:  
80% of the atoms are on the surface

A typical micellar solution containing 0.1M amphiphile has \( \sim 4 \times 10^4 \) m\(^2\) of micellar-water interfacial area per liter of solution!

For nano-size systems **surface charge effects** play a dominant role in determining the physicochemical properties (surface chemical activity) of the system as a whole.
The Electric Double Layer

\[ \psi = \psi_d \exp \left[ - \kappa x \right] \]

\( \kappa \) is termed the Debye-Hückel parameter. Its value is dependent upon the concentration and valence of electrolytic species in solution.
The electric potential depends (through $\kappa$) on the ionic composition of the medium. If $\kappa$ is increased (i.e. the electric double layer is “compressed”) then the potential must decrease.
Zeta Potential of Corundum (Al$_2$O$_3$) in Solution of Various Electrolytes
Zeta Potential: The “Effective” Surface Charge in solution

Depends upon:
  • Fundamental “surface” sites – how many, what type
  • Solution conditions – temperature, pH, electrolyte concentration

Useless to quote a zeta potential value without specifying suspension conditions
Calculation of the zeta potential

$\zeta$ is not determined directly

Most common measurement technique:
microelectrophoresis (ELS/PALS)

Electrophoretic mobility,
$U_E = V_p / E_x$

$V_p$ is the particle velocity (μm/s) and $E_x$ is the applied electric field (Volt/cm)

Relation between $\zeta$ and $U_E$ is non-linear: $U_E = 2\varepsilon\varepsilon_0 \zeta F(\kappa a)/3\eta$

The Henry coefficient, $F(\kappa a)$, is a complex function of $\zeta$

All modern commercial instruments provide both the measured electrophoretic mobility and an estimation of the zeta potential
The Effect of pH on Zeta Potential

Maximum dissociation/ionization of surface groups

ISOELECTRIC pH

Basic Surface

Acidic Surface

Zeta potential

0

pH

0

7

14

0

positive

negative

Imperative to determine ZP vs pH profile for any CMP agent prior to use
Aqueous Isoelectric Points of Silica and Alumina

The IEP can vary batch-to-batch and lot-to-lot

M. Kosmulski, *Surface Charging and Points of Zero Charge*, Boca Raton, FL, CRC Press; 2009
Zeta Potential of Two Commercial Colloidal Silicas

Always check ZP/pH profile when substituting material from different suppliers
Slurry Zeta Potential and the Polishing of Optical Glass

Glass: Corning 7940 Fused Silica (IEP: 3.5)
Polishing agents: CeO₂, ZrO₂ (monoclinic) and Al₂O₃ (nanocrystalline)

<table>
<thead>
<tr>
<th>Polishing Agent</th>
<th>IEP</th>
<th>Surface Charge at pH 4</th>
<th>Surface Charge at pH 7</th>
<th>Surface Charge at pH 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂</td>
<td>6.3</td>
<td>++</td>
<td>-</td>
<td>- - -</td>
</tr>
<tr>
<td>CeO₂</td>
<td>8.8</td>
<td>++++</td>
<td>++</td>
<td>- -</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.3</td>
<td>++++++</td>
<td>+++</td>
<td>-</td>
</tr>
</tbody>
</table>

The ZP of the polishing slurries varies with solution pH
♀ positive or negative depending upon the metal oxide IEP
The glass surface roughness depends upon the difference in fluid pH and the IEP of the polishing agent. The more positive the difference, the smoother the surface.

Solution pH must be > the polishing agent IEP
Choose CMP agent whose IEP < Fluid pH
Zeta Potential of Non-oxides

The ZP value affected by presence of surface impurities and contamination

\[
\text{Si}_3\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 3\text{SiO}_2 + \text{NH}_3
\]

\[
\text{(SiOH}_2\text{)}^+ \leftarrow \text{SiOH} \rightarrow \text{(SiO)}^-
\]
In Conclusion

Surface Charge is a fundamental parameter that impacts the performance of CMP agents.

The polishing efficiency of CMP slurries is dependent upon not just the metal oxide particle size but also the hydroxyl [OH] concentration and state of dissociation.

The Zeta Potential of aqueous suspensions of metal oxide polishing agents critically impacts polishing efficiency. It should be a basic QC measurement for all incoming material.

In practice, either the CMP IEP must be < fluid pH or the solution pH must be adjusted to a value > CMP IEP.
Q&A

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Thank you