Colloidal processing of Pb(Zr,Ti)O₃, Part I-Pb dissolution

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The dissolution behavior of aqueous Pb(Zr,Ti) O₃(PZT) suspensions were studied by Atomic Adsorption (AA) and Inductively Coupling Plasma (ICP) spectroscopies, specially emphasizing the change of solution acidity within pH 2 to 12, the effects of polymeric dispersant, and comparing with the dissolution behavior of PbO. The iso-electric-point (IEP) of a 2.0 wt % PZT solution was measured and compared to the minimal dissolution case (less than 10 ppm) to be in the range of pH 7 to 10. The effects of one dispersants, poly (α-N,N-dimethyl-N-acryloxyethyl) ammonium ethnate acrylamide (PMAA/DAAE) was investigated in comparison with a commercial anionic dispersant, an ammonium salt of polymethylacrylic acid (PMAAN). A possible dissolution model and the thickness of the Pb depletion zone on PZT particles are proposed based on the experimental observation.

Key words: PZT, dissolution, iso-electric point, PMAA/DAAE, PMAAN, depletion zone.

Introduction

Pb(Zr,Ti)O₃ (PZT) is one of the important electrical ceramics due to its unique piezoelectric properties. However, PZT powder is rarely dispersed in aqueous solution due to the dissolution of some of the Pb content in acidic conditions [1]. The pollution by and non-stoichiometry of Pb in PZT requires the use of Pb-containing piezoelectric ceramics in a non-polar organic solvent system. However, most of the organic solvents are not friendly to the environment. Recent environmental regulations have limited ceramic processing without using a toxic organic solvent. An aqueous-based process seems to be the final solution. The processing of PZT in water is a much-debated issue.

Several piezoelectric applications, such as accurator and ultrasonic generator/receiver, have been developed, and have become more sophisticated [2]. The elements are not only designed in a complex shape, but require highly precise dimensional control. Therefore, final machining to achieve the final dimensions is a major portion of the manufacturing cost. In order to reduce the volume of machining, a precise molding method was developed by using aqueous suspensions [3].

In this research, the dissolution of Pb ions from a PZT slurry was investigated and compared to that of pure PbO powder. The effects of acidity (the pH) of the slurries and two dispersants with different functional groups were also studied. These dissolution results can be a technical indication of PZT processing in aqueous solution.

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Experimental Procedure

Two powders were tested; one was high purity (99.9%) PbO powder (Thye Ming Industrial, Co. Ltd., Taiwan) with an average grain size of 0.4 μm. The PZT powder was prepared as per previous work [3] with the composition PbO:ZrO₂:TiO₂=68.27:11:20.73 wt%. The average grain size and the crystalline phase of the PZT powder were 1.0 μm and the tetragonal phase, respectively.

Two dispersants, an ammonium salt of polymethyl acrylic acid (PMAAN, Venderbelt Co., USA) and poly (α-N,N-dimethyl-N-acryloxyethyl) ammonium ethnate acrylamide (PMAA/DAAE, the chemical was supplied by Professor Hsu from the Normal University, Taipei, Taiwan) were prepared. PMAAN at a molecular weight (M_w) 13,000-15,000 was dissolved in water with a solid content of 29 mass%. PMAA/DAAE is an ampholeric polymer with two major functional groups, -NH₄ and -COOH with a molecular weight between 30,000-80,000 g/mol.

In order to prevent the precipitation of Pb ions [4], the pH of the slurries was adjusted between pH 2-12 by regent grade NaOH and HNO₃ solutions. 2.0 mass% of PbO powder was dispersed in the solution, which was at a specified pH (initial pH) value. However, 2-20 mass% of the PZT powders were added to slurries in order to compare the effects of dissolving Pb ions. The slurries were always aged at 40 °C.

The ζ-potential of the PZT powder in an aqueous suspension was measured by a Zetameter (Model 501 Lazer Zee Meter, Pen Kem, Inc. NY, USA). The slurry was prepared as previously mentioned; only the PZT concentration of the suspension was 300 ppm. After 24 h aging, the ζ-potential of the powder in suspension

was measured to determine the potential at equilibrium.

The concentration of the dissolved Pb in the slurries was tested by Atomic Adsorption spectroscopy (AAnalyst 800, Perkin Elmer Instru., USA) and Inductively Coupled Plasma emission spectroscopy (ICP, JY24, JOBIN YVON, France). In order to obtain clean solutions (supernatant), solid particles had to be separated from slurry. The slurries for the test were centrifuged (HERMLE Z380, Germany) at 5000 rpm for 13 minutes. Standard solutions of Pb^{2+} in various concentrations for calibration were diluted from 1000 ppm solution (regent grade, MERCK).

It is known that PbO dissolves in acidic solution extensively [4]:

$$Pb^{2+}+2OH^- \leftrightarrow Pb(OH)_2 \ K=6.47\times10^{15} \text{ at } 40 \text{ °C} \quad (1)$$
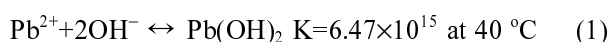
In fact, Pb ions can have several ionic forms in aqueous solution, $Pb(OH)^+$, $Pb(OH)_3^-$, or may precipitate as a white powder of $Pb(OH)_2$ as shown in equation 2. Therefore, the supernatant needs treatment before ICP measurement so to keep the Pb-species in the dissolved condition. The reaction is shown below. The amount of the NaOH solution needed [5] was 3 ml in every 5 ml supernatant:

$$Pb(OH)_2+OH^- \leftrightarrow +Pb(OH)_3^- \quad (2)$$
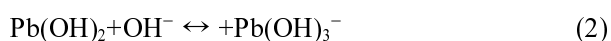
Results and Discussion

Dissolution of PbO

The concentration of dissolved Pb-species in PbO suspensions is shown in Fig. 1. The results show that PbO can be apparently dissolved not only in acidic (pH=2), but in basic (pH=12) solutions. The dissolution of the PbO powder in various pH solutions takes at least 10 h to reach equilibrium. Among the test samples, the lowest dissolved concentration is in the solution at pH=10.

Oxide powder usually has the lowest dissolved concentration near the iso-electric point (IEP). The colloidal particles with least charge on their surfaces show an agglomerated state. Away from the IEP, the particle surface exerts a repulsive force which keeps the particles separated. Therefore, the PbO slurry can be in a dispersed condition compared to that at the IEP. The latter will have less available surface area and will take a longer time to reach equilibrium due to the agglomerated state. This implies that the IEP of PbO may be close to pH=10.

The dissolution of Pb ionic species is similar to that of Y^{3+} dissolving from Y-TZP powder [6]. The surface charging reactions can be shown as below:

$$PbO+H^+ \leftrightarrow PbO\text{-}H^+ \ pH \leq iep \quad (3a)$$

$$PbO+OH^+ \leftrightarrow PbO\text{-}OH^- \ pH \geq iep \quad (3b)$$
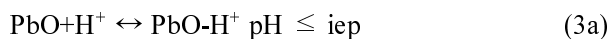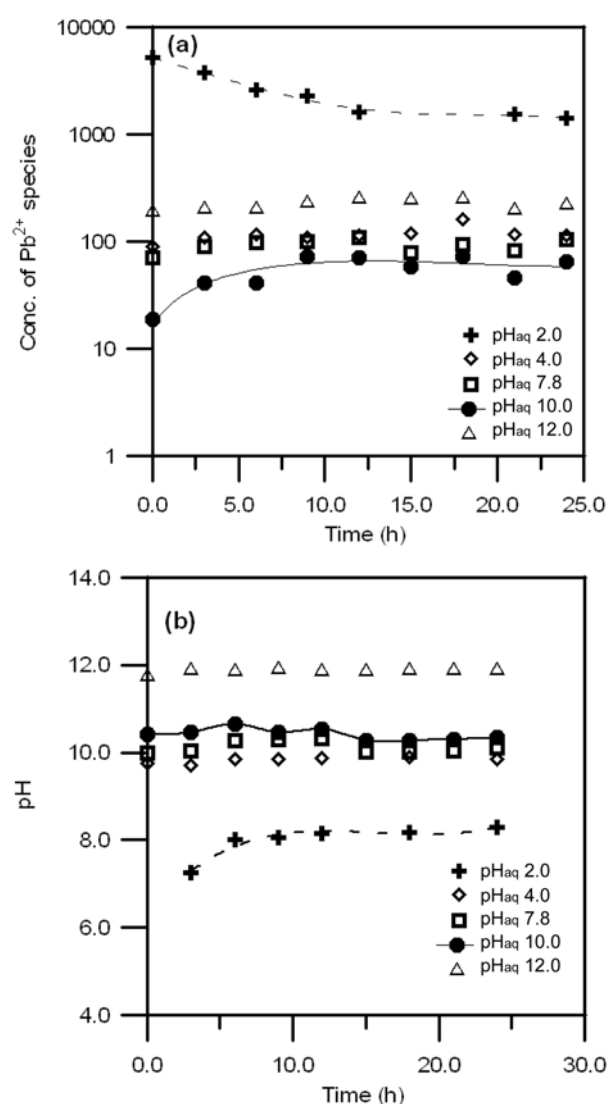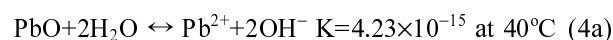
and it is known that [7]:

Fig. 1. (a) The concentration of Pb^{2+} and (b) the change in pH with time in 2 wt% PbO suspension at different pH_{aq}. The suspensions were aged at 40 °C.

$$PbO+2H_2O \leftrightarrow Pb^{2+}+2OH^- \ K=4.23\times10^{-15} \text{ at } 40°C \quad (4a)$$

$$\text{or } PbO+2H^+ \leftrightarrow Pb^{2+}+H_2O \quad (4b)$$

The solution in pH_{aq} less than 10 will have the reactions, which form either a $PbO\text{-}H^+$ on the particle surface or dissolve Pb^{2+} in solution. These reactions, eqs. (3a) and (4a) make the solution more alkaline due to the adsorption of H^+ and the dissolution of Pb^{2+}.

The acidity change of the slurries after mixing the PbO powder is shown in Fig. 2. In acidic conditions, the PbO reacts with H^+. The concentration of H^+ and OH^- varied over 6.5 orders. The reactions at pH>10 are more complex. The dissolvable Pb species are sensitive to the concentration of OH^-, as shown in eq. (2). There is possibly the formation of $Pb(OH)_3^-$ if additional OH^- is added in the slurry at pH =12. The results of Figure 2 show that no apparent reaction is proceeding.
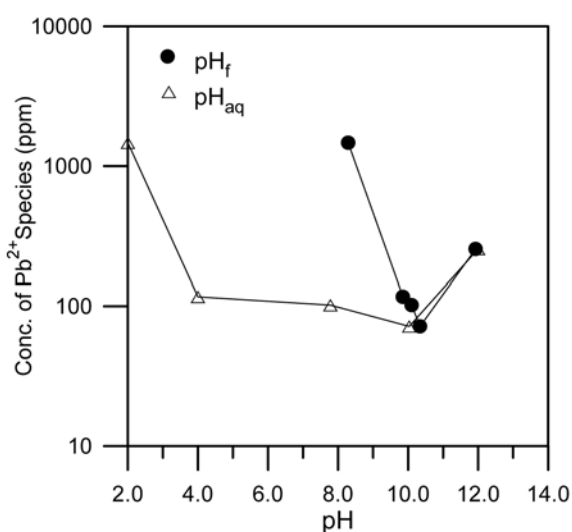
Fig. 2. The relation of the concentration with pH_{aq} and pH_f in 2 wt% PbO suspension aged at 40 °C for 24 h.

Dissolution of PZT

Figure 3 shows the results of 2 wt% PZT powder dispersed in aqueous solution. The variation of the concentration of dissolvable Pb species and the pH value show a similar trend as that of the PbO slurries. The Pb concentration in the PZT slurries is about 50 times less than that in the PbO slurry. The dissolution of Pb species gets stabilized within 5 h and shows the lowest concentration, < 1 ppm, in the solution of pH=10.

A similar dissolution test was also conducted in various organic solvents, including toluene, heptane, and MEK. The result for the Pb concentration, as shown in Table 1, was below the detectable level (<0.1 ppm).

The molar and mass ratio of the PbO content in PZT is 0.32 and 0.68, respectively. The measured dissolution of Pb from PZT powder is far less than the case of PbO in aqueous solution. This implies that the perovskite structure fixes Pb^{2+} between TiO_6 octahedrons, and greatly reduces the amount of Pb dissolution.

Figure 3(b) shows the pH of PZT slurries changing with the time. It was noted that the pH of the PZT slurries reduced as soon as the powder was added, as appeared at time=0. However, previous results (Fig. 3(a)) reported that except for the slurry at pH=12, the rest showed very minor Pb dissolution. The reduction of pH value in the initial stage should be a type of surface reaction of PZT with OH^-, and the pH of the slurry gradually increases as Pb dissolves which takes more than 10 h to reach equilibrium.

Figure 4 shows the concentration of dissolved Pb species as a function of pH_{aq} and pH_f. In an acidic solution (pH<7), the pH_f values is higher than the pH_{aq} of the solution, which might be due to the protonization of the PZT surface, as shown in eq. (1). The change in pH (ΔpH) is less apparent for PZT slurries than for PbO slurries.
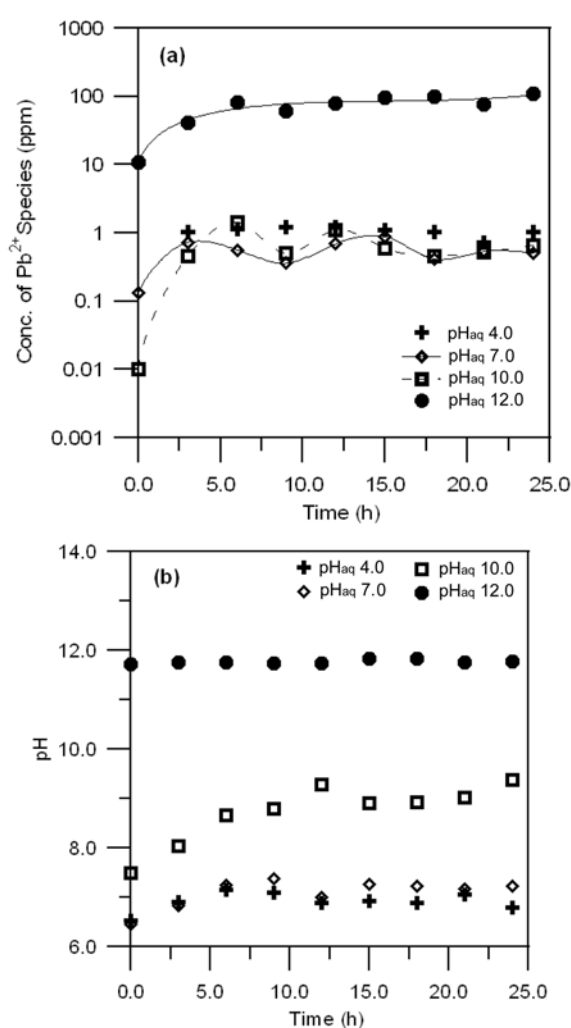

Fig. 3. (a) The concentration of Pb^{2+} and (b) the change in pH with time in 2 wt% PZT suspension at different pH_{aq}. The suspensions were aged at 40 °C.

Table 1. Concentrations of Pb dissolved from PZT powder in various dispersion systems

System for Pb dissolution test	Pb conc. (ppm)
H_2O (pH=7)	1.0
Toluene	0.0
Heptane	0.0
MEK	0.0

The dissolution of Pb ions occurs from the surface layer of PZT similar to Ba ions from $BaTiO_3$ powder [8, 9]. A depletion layer is formed by the diffusion process. The distribution of Pb near the particle surface can be described by Fick's second law. However, a simpler approach is to assume that the dissolved Pb is coming mainly from the skin layer.

Figure 5 shows the ζ-potential of PZT powder changing with the pH_i and pH_f of the suspensions. The IEP of the PZT is at pH=5, which is smaller than the IEP of PbO ($\sim pH=10$) previously mentioned. The main
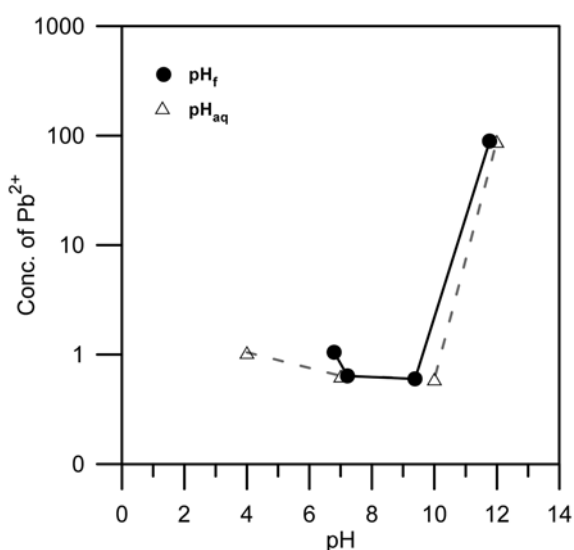
Fig. 4. The relation of the concentration with pH_{aq} and pH_f in 2 wt% PZT suspension aged at 40 °C for 24 h.
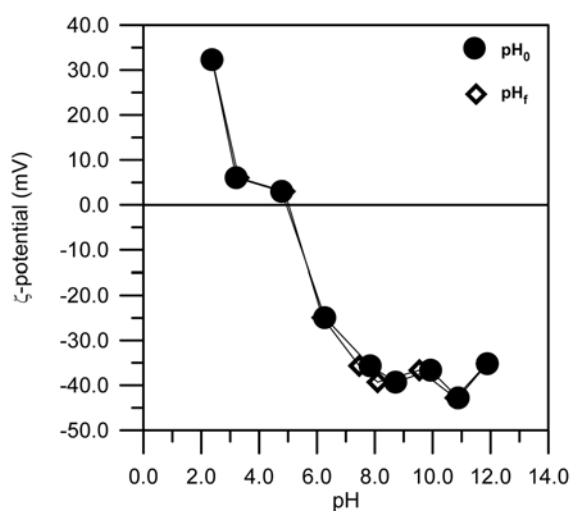

Fig. 5. Zeta-potential plotted against pH of PZT suspension with 300 ppm concentration. The pH_o and pH_f mean the pH of aqueous solution before the addition of PZT powder and 24 h after the addition of powder respectively.

reason might be due to the different solid loading of the suspensions measured. To reach an equilibrium concentration in the solution, the amount of Pb^{2+} dissolved from the powder surface should be the same for all suspensions. As the solid loading decreased, the thickness of the depletion layer of Pb on PZT increased, and the surface of the powder was rich in Zr- and Ti-oxides, which showed an IEP between pH 5-6.

Effects of Dispersant

The effect of two polyelectrolyte dispersants, PMAA/DAAE and PMAAN were investigated and reported in Fig. 6. The pH_{aq} of two dispersants added in H_2O was 5.5 and 8.6, respectively. The two polymeric dispersants act as buffers for pH control. The acidity of the
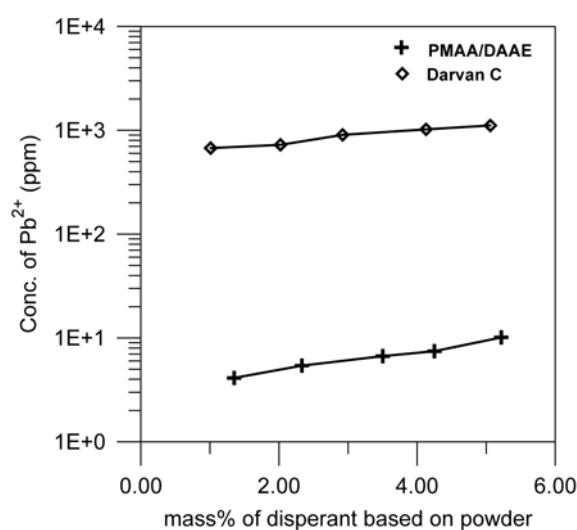

Fig. 6. The concentration of Pb^{2+} in 20 wt% PZT solutions with various amounts of dispersants aged at 40 °C for 24 h.

two systems after 20 wt% PZT powder was added did not apparently change. The pH of the slurry is close to that of the solution with the PZT powder. However, some dissolution of Pb^{2+} (1000 ppm) for the PMAAN system was noted. This is several orders greater than the concentration of dissolvable Pb (10 ppm) in the PMAA/DAAE system. The amount of Pb dissolution in PZT slurries is between 1 to 10 ppm, which is still higher than the requirement (< 0.05 ppm) due to environmental regulations.

Conclusions

PZT does not dissolve any Pb in selected organic solvents, but is dissolvable not only in an acidic aqueous solution, but also in a strong basic (pH>10) solution. During the dispersion of the powders, the increase of pH in the acidic condition is related to the dissolution of Pb species and to the surface adsorption of H^+. The decrease of pH in a basic solution is due to the formation of $Pb(OH)_2$ precipitates and $Pb(OH)_3^-$.

The minimal dissolution of PbO and PZT in solutions with 2 wt% solid loading is 100 ppm and 1 ppm, respectively. This takes place near the IEP of the powder system. The IEP of PZT in the suspension with 300 ppm solid loading is at pH=5, which is smaller than that of the solutions with 2 wt%. This is because of the depletion of Pb from the surface of PZT in aqueous suspension. The concentration of dissolvable Pb species in a PZT slurry with PMAA/DAAE is 3 orders less than that in the PMAAN system.

Acknowledgement

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