

Economic Fabrication of Membrane Materials

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INTRODUCTION

Inorganic, asymmetric membranes have many potential applications in fossil energy systems such as H₂ recovery from mixed gas streams, H₂S removal, efficient O₂ combustion, aromatic upgrading, fuel reforming, and conversion of natural gas to syngas. The current class of ceramic monolithic oxygen and hydrogen membranes have relatively low flux due to high membrane thickness (> 100 μm). In order to reduce the footprint of the separation device while increasing flux, thinner membranes are required. Thin membranes, however, maybe too fragile to function as self-supported structures in high pressure, fossil environments. As a result, porous supports are used to impart the necessary mechanical behavior, while also allowing for fluid flow through the pore network to the membrane. Typically, the membrane and support are manufactured from the same material (i.e., a rare-earth based ceramic), in order to assure that they have the same coefficient of thermal expansion (CTE) and thus, eliminate complications that may arise when cofiring. However, the expense associated with using larger quantities of the rare-earth based material, coupled with the need for glass or glass-ceramic seals, eliminates the long-term commercial viability of such devices.

In order to utilize inorganic membranes in a wide array of energy applications, low-cost fabrication methods must be developed that utilize inexpensive membrane and support materials. Calcium ferrite-based ceramics with brownmillerite structure have been recently identified as excellent candidates for dense, asymmetric oxygen transport membranes. The base composition (Ca₂Fe₂O₅) elicits strong, mixed conducting behavior and is easily doped, e.g., with Ga, Al, Cr, Co, Ti, and Ni, to improve the conductivity via an oxygen vacancy diffusion mechanism and mechanical stability. Furthermore, metallic supports with high temperature capabilities (1300 °C) have great potential for improving the mechanical strength and reducing the material costs. The use of metallic membranes also facilitates the use of simple seals, such as brazes, thus avoiding the need for glass or glass-ceramic seals.

Aqueous colloidal processing of ceramic suspension precursors offers a low cost approach for producing uniform, ceramic membranes on porous metallic supports via a simple dip coating process. This approach has been demonstrated in many multi-disciplinary areas such as coatings (paints,

glazes), fabrication of monolithic components (casting, deposition), and emulsions (gels, food additives, cosmetics). Control of the suspension rheological behavior is paramount to produce high quality coatings and can be accomplished by tailoring interparticle (or surface) forces. In aqueous-based suspensions, long-range attractive van der Waals forces are ubiquitous and must be balanced by repulsive forces to tailor the desired degree of colloidal stability. For example, ionizable polymeric dispersants (i.e. polyelectrolytes) are commonly used to modify the surface of particles to impart repulsive electrosteric interparticle forces.^{1,2} In aqueous colloidal processing of calcium ferrite suspensions, however, additional complications arise due to particle hydrolysis and hydration (cementitious) reactions. Hydrolysis occurs as the particles undergo partial dissolution and the release of multivalent ions (e.g. Ca^{2+} , Al^{3+} , and Fe^{3+}) into solution. The rising ionic strength and the presence of multivalent ions in solution mitigate repulsive forces imparted by adsorbed (pure) polyelectrolyte layers.³ Calcium ferrite also elicits strong cementitious behavior in aqueous suspension (note, it is one of the four primary phases in Portland cement).⁴ Hydration reactions occur when hydrolyzed ions react to form new solid phases. These phases typically form at the particle-particle contacts resulting in irreversible hardening and ultimately, set of concentrated suspensions.

In the current study, aqueous calcium ferrite suspensions are developed for use as precursors in a dip-coating process with select chemical additions to impart stability to the system. Additions of oxalic acid and citric acid are studied based on claims that they retard hydrolysis⁵ and hydration,⁴ respectively. Addition of a novel, polyelectrolyte-based dispersant with comb polymer architecture is also studied based on success in other suspensions where hydrolysis is observed, including barium titanate³ and Portland cement.⁶ Zeta potential experiments are carried out to characterize the surface of calcium ferrite particles in dilute aqueous suspension. Furthermore, the set time and rheological behavior are characterized for concentrated suspensions (45-55 vol% solids) formulated with a wide range of oxalic acid, citric acid, and comb polymer addition. Concentrated calcium ferrite suspensions suitable for a dip-coating process are identified and used to form membranes on porous metallic supports. The coated supports are sintered in a flowing argon atmosphere over a wide temperature range. Results show that the suspension structure and rheology can be carefully controlled to govern the quality of green and ultimately, dense membranes.

DISCUSSION OF CURRENT ACTIVITIES

MATERIALS SYSTEM

$\text{Ca}_2\text{Fe}_2\text{O}_5$ (Praxair) with an average particle size of 1.0 μm determined using dynamic light scattering (LA-700, Horiba Instruments Incorporated, Irvine, CA) and a surface area of 1.47 m^2/g , determined using nitrogen adsorption BET (Autosorb-1, Quantachrome Instruments, Boynton Beach, FL), was the ceramic powder used in this study. Oxalic acid and citric acid were obtained and used to modify the reactivity of the $\text{Ca}_2\text{Fe}_2\text{O}_5$ powder in water. Note, these molecules are very similar in chemical structure (i.e., citric acid differs from oxalic acid by only one hydroxycarboxylic acid group located between the two carboxylic acid groups) (see Fig. 1). The dispersant in this study was a poly(acrylic acid)-poly(ethylene oxide) copolymer with comb-like molecular architecture (i.e., it has an anionic, poly(acrylic acid) (PAA) backbone and charge-neutral, poly(ethylene oxide) (PEO) teeth) (see Fig. 1). The PAA/PEO copolymer had a number and weight average molecular weight of 23,400 g/mole and 8,330 g/mole, respectively, as determined by GPC analysis.

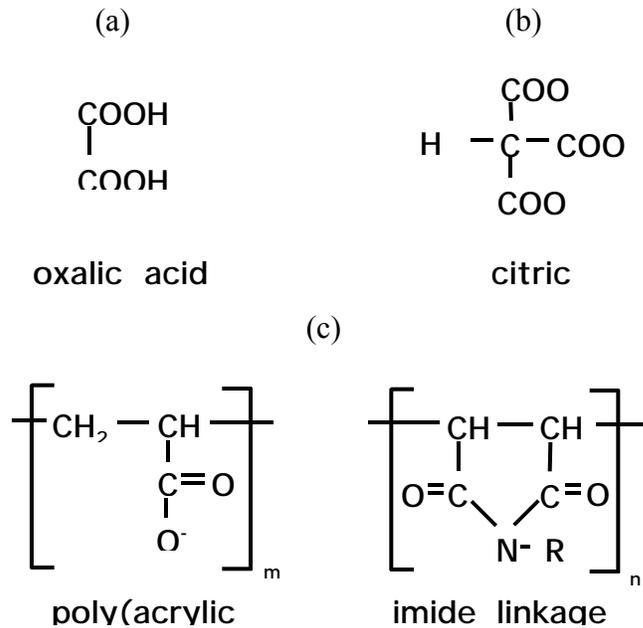


Fig. 1. The chemical structure of (a) oxalic acid, (b) citric acid, and (c) PAA/PEO. Note, in (c) $\text{R} = (\text{CH}_2\text{CH}_2\text{O})_x\text{-CH}_3$, i.e., poly(ethylene oxide), which is grafted onto the poly(acrylic acid) backbone at random intervals through the imide linkages ($m = 59$, $n = 8$, $x = 45$).

ZETA POTENTIAL

Zeta potential measurements were carried out on the $\text{Ca}_2\text{Fe}_2\text{O}_5$ particles in dilute aqueous suspension using capillary electrophoresis (Zetasizer 3000HS, Malvern Instruments Ltd., Worcestershire, UK). Dilute suspensions (10^{-3} vol% solids) were prepared by adding the appropriate amount of powder to aqueous, KNO_3 solutions (0.01 M) of varying pH ranging from 2 – 11. The solutions were adjusted to the appropriate pH using stock solutions of nitric acid or ammonium hydroxide. The suspensions were ultrasonically treated for 2 min. to break up soft agglomerates prior to measurement. As shown in Fig. 2, the isoelectric point (IEP) was observed at pH 8, which is within the range of literature values for Fe_2O_3 (pH 6-9) (Ref. 7).

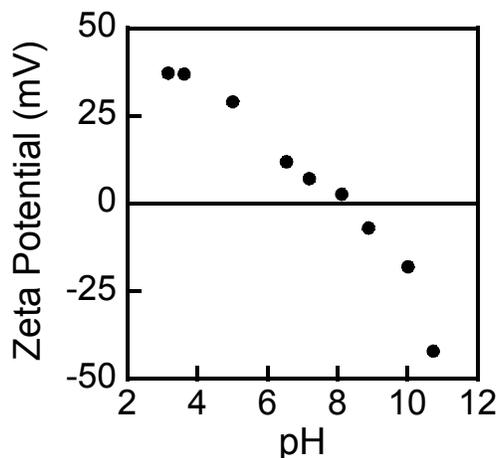


Fig. 2. Zeta potential as a function of pH for $\text{Ca}_2\text{Fe}_2\text{O}_5$ particles in dilute, aqueous suspension (10^{-3} vol% solids).

This result is consistent with the surface behavior of inorganic particles that undergo hydrolysis, i.e., Ca^{2+} dissolves into solution leaving behind an Fe-rich surface. We have extensively studied such behavior for another important inorganic membrane material— BaCeO_3 . In concentrated, Ba-based perovskites suspensions, little Ba^{2+} dissolution is necessary from the individual particles to obtain Ba^{2+} saturation in the solution medium. As a result, the BaCeO_3 is Ba-rich and has an IEP at high pH (~10.5-11). In dilute solution, however, significant Ba dissolution occurs from the individual particles to saturate the solution medium. As a result, the zeta potential versus pH profile strongly resembles that of CeO_2 , as shown in Fig. 3. Interestingly, an instability is observed at a pH range of 7-9. Below this regime, some dissolution of Ce^{3+} likely occurs as it is the stable species in aqueous solution predicted in the cerium Pourbaix diagram (see Fig. 4). Above this regime, however, $\text{Ce}(\text{OH})_3$ is the stable phase. The instability reflects the transition region where Ce^{3+} reacts with OH^- to form $\text{Ce}(\text{OH})_3$ on the particle surfaces. Identical behavior is observed with some Y_2O_3 substitution (20%), which is commonly done to create oxygen vacancies in the BaCeO_3 system.

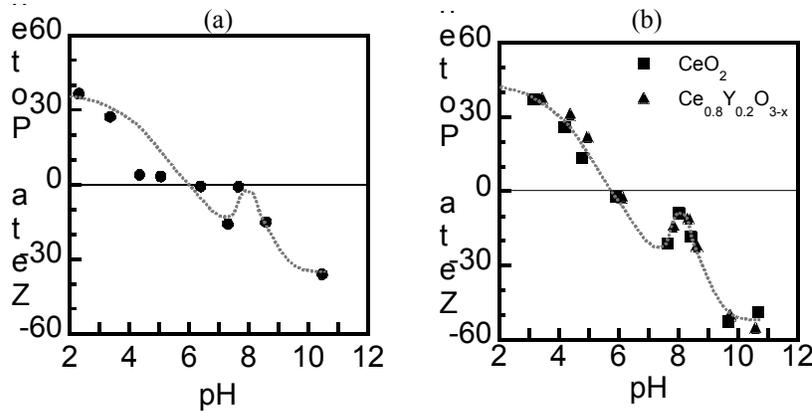


Fig. 3. Zeta potential as a function of pH for (a) BaCeO_3 and (b) CeO_2 -based particles in dilute, aqueous suspension (10^{-3} vol% solids).

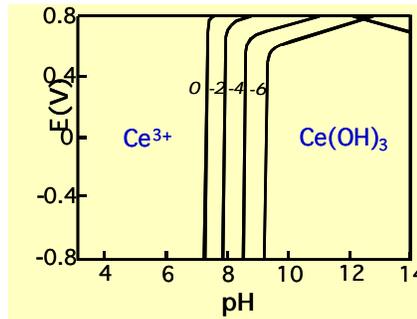


Fig. 4. The cerium Pourbaix diagram.

SETTING BEHAVIOR

Concentrated $\text{Ca}_2\text{Fe}_2\text{O}_5$ suspensions (45-55 vol% solids) were fabricated by combining an appropriate amount of $\text{Ca}_2\text{Fe}_2\text{O}_5$ powder with aqueous solutions of varying oxalic acid, citric acid, and PAA/PEO concentration. The suspensions were ultrasonically treated for 5 min (60 Hz) to break up soft agglomerates and mixed on a shaker table to achieve equilibrium. A needle penetration test was utilized to determine the set time for concentrated $\text{Ca}_2\text{Fe}_2\text{O}_5$ suspensions (45 vol% solids) after

initial $\text{Ca}_2\text{Fe}_2\text{O}_5$ powder contact with pure water, aqueous oxalic acid solution (10 mg per m^2 $\text{Ca}_2\text{Fe}_2\text{O}_5$), and aqueous citric acid solution (10 mg per m^2 $\text{Ca}_2\text{Fe}_2\text{O}_5$). In pure water and aqueous oxalic acid solution, setting occurred 5-10 min after initial $\text{Ca}_2\text{Fe}_2\text{O}_5$ /water contact; however, setting did not occur until 17 days after $\text{Ca}_2\text{Fe}_2\text{O}_5$ contact with aqueous citric acid solution. Strong set retardation imparted by citric acid can be attributed to its additional hydroxycarboxylic acid group as compared with oxalic acid. It has been demonstrated that hydroxycarboxylic acid and carboxylic acid groups form strong and weak complexes, respectively, with multivalent cations in solution.⁸ Strong hydroxycarboxylic acid- Ca^{2+} complexes are highly stable and thus, prevent Ca^{2+} ions from participating in hydration reactions to form hydrated solid phases. As a result, setting behavior is delayed until enough free Ca^{2+} ions become available from further $\text{Ca}_2\text{Fe}_2\text{O}_5$ dissolution.

RHEOLOGICAL BEHAVIOR

Rheological measurements were carried out on concentrated suspensions using a controlled-stress rheometer (Rheometric Scientific SR5, TA Instruments, New Castle, DE) fitted with concentric cylinder geometry. Prior to measurement, the suspensions were presheared at a rate of 200 s^{-1} for 5 min and then allowed to equilibrate for 15 min. Furthermore, a specially designed solvent trap was used to minimize the evaporation of water. In this way, variations in sample handling were minimized to ensure reproducibility of the data. Stress viscometry measurements were carried out by ramping an applied shear stress (logarithmically) from 0.025 to 200 Pa. A delay time (i.e., the time between two consecutive data acquisition events) of 1 min was used in this study. After repeating the preshear procedure mentioned above, storage modulus (G') measurements were carried out by ramping an oscillatory shear stress (logarithmically) from 0.025 to 200 Pa at a constant frequency of 1 Hz. All rheological measurements were performed at a constant temperature of 25°C.

Results for concentrated $\text{Ca}_2\text{Fe}_2\text{O}_5$ suspensions (constant citric acid addition, 10 mg/ m^2 $\text{Ca}_2\text{Fe}_2\text{O}_5$) are shown in Figs. 5-6. The apparent viscosity is plotted as a function of applied shear stress in Fig. 5 for suspensions of varying PAA/PEO addition (constant solids loading, 45 vol%) and varying solids loading (constant PAA/PEO addition, 2 mg per m^2 $\text{Ca}_2\text{Fe}_2\text{O}_5$). The degree of shear-thinning decreased with increasing PAA/PEO concentration until it was minimized at 2 mg PAA/PEO per $\text{Ca}_2\text{Fe}_2\text{O}_5$. However, it was not possible to completely eliminate shear-thinning behavior, which is indicative of a net attractive interparticle interaction. By increasing the solids loading, i.e., the number of attractive particles, shear-thinning behavior increased as expected.

The elastic modulus is plotted as a function of applied shear stress in Fig. 6 for suspensions of varying PAA/PEO addition (constant solids loading, 45 vol%) and varying solids loading (constant PAA/PEO addition, 2 mg per m^2 $\text{Ca}_2\text{Fe}_2\text{O}_5$). Solid-like behavior, indicative of colloidal gels, was observed. The linear elastic modulus and yield stress increased with decreasing PAA/PEO concentration (i.e., increasing net interparticle attraction) and increasing solids loading (i.e., increasing concentration of attractive particles). These parameters can be adjusted over several orders of magnitude to fabricate $\text{Ca}_2\text{Fe}_2\text{O}_5$ suspensions with a wide-range of dip-coating behavior.

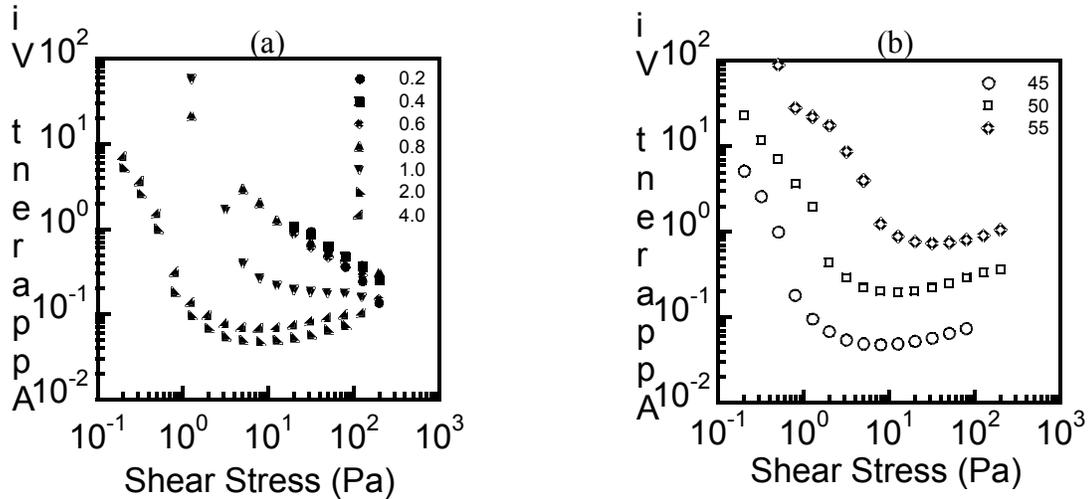


Fig. 5. Apparent viscosity as a function of shear stress for (a) 45 vol% $\text{Ca}_2\text{Fe}_2\text{O}_5$ suspensions with 10 mg citric acid per m^2 $\text{Ca}_2\text{Fe}_2\text{O}_5$ and varying PAA/PEO concentration (0.2 – 4.0 mg per m^2 $\text{Ca}_2\text{Fe}_2\text{O}_5$) and (b) $\text{Ca}_2\text{Fe}_2\text{O}_5$ suspensions with 10 mg citric acid and 2 mg PAA/PEO per m^2 $\text{Ca}_2\text{Fe}_2\text{O}_5$ and varying solids loading (45 – 55 vol% solids).

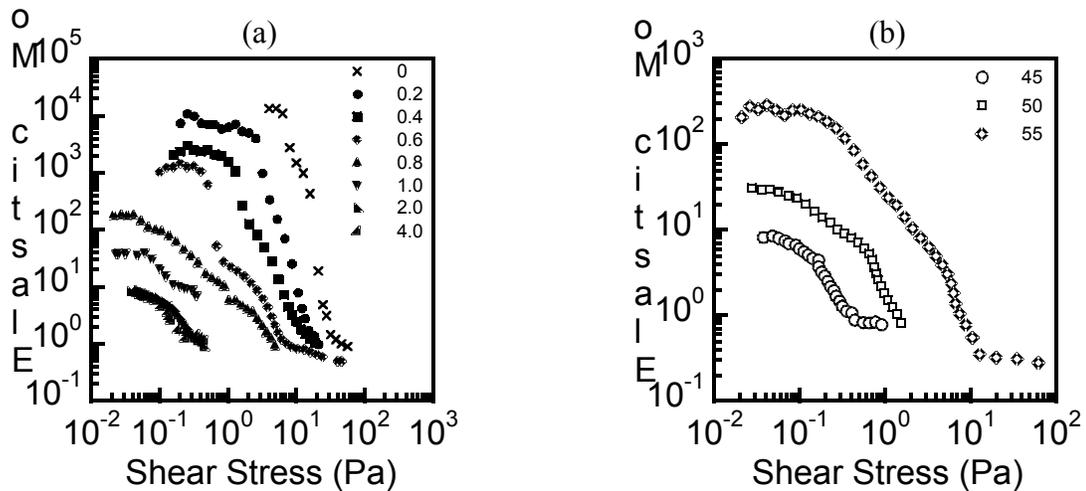


Fig. 6. Elastic modulus as a function of shear stress for (a) 45 vol% $\text{Ca}_2\text{Fe}_2\text{O}_5$ suspensions with 10 mg citric acid per m^2 $\text{Ca}_2\text{Fe}_2\text{O}_5$ and varying PAA/PEO concentration (0.2 – 4.0 mg per m^2 $\text{Ca}_2\text{Fe}_2\text{O}_5$) and (b) $\text{Ca}_2\text{Fe}_2\text{O}_5$ suspensions with 10 mg citric acid and 2 mg PAA/PEO per m^2 $\text{Ca}_2\text{Fe}_2\text{O}_5$ and varying solids loading (45 – 55 vol% solids).

MEMBRANE FORMATION ON METALLIC SUPPORTS

Porous, stainless steel tubular supports were obtained (9.78 mm ID, 11.05 mm OD) and sectioned into ~ 6.5 mm lengths. The sectioned tubes were ultrasonically cleaned in ethanol for 10 min and dried in ambient conditions. Rubber stoppers were inserted before dipping to prevent the suspension from coating the inner diameter of the support. The tubes were dipped into 45, 50, and 55 vol% $\text{Ca}_2\text{Fe}_2\text{O}_5$ suspensions with 10 mg citric acid and 2 mg PAA/PEO per m^2 $\text{Ca}_2\text{Fe}_2\text{O}_5$. The substrates were dipped at a rate of 85.7 mm/min, submerged for 10 sec, and withdrawn at a rate of 85.7

mm/min. Coated tubes were dried under ambient conditions and sintered at varying temperature in 300 cm³/min flowing argon.

Stainless steel supports were dipped into Ca₂Fe₂O₅ suspensions (2 mg PAA/PEO per m² Ca₂Fe₂O₅) of varying solids loading and the resulting membranes are displayed in Fig. 7. The rheological behavior of each suspension had strong impact on the resulting membrane quality. Uniform membranes were obtained from suspensions with solids loading ranging between 45 – 50 vol% (linear elastic moduli (G_0) between 10 - 30 Pa), although the membrane thickness increased with solids loading because of the increase in G_0 . Non-uniform membranes, with thick sections that cracked during drying, were obtained from suspensions of 55 vol% solids that had G_0 of 300 Pa.

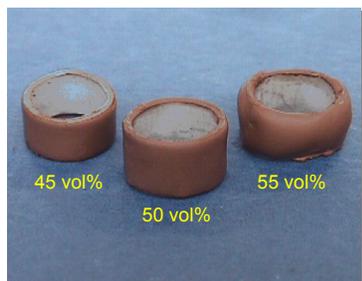


Fig. 7. Ca₂Fe₂O₅ membranes on the outer diameter of stainless steel, tubular supports.

The Ca₂Fe₂O₅ membranes (from 45 and 50 vol% suspension precursors) and stainless steel supports were co-sintered over a wide range of temperatures in a flowing argon atmosphere. A reducing environment was required to prevent oxidation of the metallic support. At 1200°C and above, the membrane and metallic support reacted and a liquid phase formed. Ca₂Fe₂O₅ membranes densified between 900 and 1100°C, although cracking was observed that increased with increasing sintering temperature and membrane thickness. These parameters are proportional to residual stresses generated within the membrane due to shrinkage against the metallic support. At 800°C, cracking was eliminated from the thinnest Ca₂Fe₂O₅ membrane (from 45 vol% suspension), although it is not known if complete densification occurred. In future work, we will minimize the thickness to obtain dense, crack-free membranes.

CONCLUSIONS

Aqueous colloidal processing of ceramic suspensions offers a low-cost approach of forming inorganic membranes on porous, metallic supports. It has been demonstrated that this approach is feasible even for membrane materials that undergo deleterious reactions with water by the use of key additives such as citric acid and PAA/PEO comb polymer dispersants to promote long-term suspension stability. Furthermore, it has been demonstrated that it is possible to co-sinter Ca₂Fe₂O₅ membranes on stainless steel supports, although more work is required to fine tune the temperature and coating thickness required to obtain dense, crack free coatings.

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