Quarterly Management Report

WBS Element	Project Title	Contract Number	Contract Start	Contract End
ORNL-3H	Economical Fabrication of Membrane Materials	FEAA028		

Performer Name and Address	Principal Investigator(s)
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BUDGET AND COST REPORT

Prior Year Funds [$K]	104
Total Current Year Commitment $K]	200
Projected Current Year Costs [$K]	304

	O	N	D	J	F	M	A	M	J	J	A	S
Planned Costs	25	50	75	100	125	150	175	200	225	250	275	304
Actual Costs	47	65	78									
Variance	(22)	(15)	(3)	100	125	150	175	200	225	250	275	304

MILESTONE REPORT

Milestone Designation	Milestone Description	Due Date	Revised Due Date	Completion Date
1	Develop high-temperature porous metallic support using 400 series stainless steel	04/01/04		
2	Develop understanding of colloidal properties of barium cerate	12/30/03		12/30/03
3	Demonstrate deposition of ceramic membranes on metallic supports	09/30/03	06/30/04	
4	Demonstrate proof-of-concept for sintered membrane on metallic support	09/30/04		

TECHNICAL HIGHLIGHTS

Concentrated, aqueous suspensions of doped barium cerate and barium cerate zirconate have been fabricated for use in a dip-coating process that will allow for low cost production of hydrogen separation membranes on metallic substrates.

We have studied the behavior of aqueous suspensions comprised of barium cerate (Ba0.98Ce0.8Y0.2O3-x) and barium cerate zirconate (Ba0.98Ce0.6Y0.2Zr0.2O3-x) particles. Zeta potential experiments were carried out in order to characterize the surface of these particles in aqueous suspension using another barium-based perovskite, i.e.,BaTiO3, as a benchmark. In addition, concentrated suspensions (~ 45 vol%) suitable for a dip-coating process were fabricated using a novel dispersant.

Zeta potential measurements were carried out as a function of pH for BaTiO3 suspensions of 10-3 vol% and 1 vol% solids using capillary electrophoresis (Zetasizer 3500HS, Malvern Instruments Ltd.) and electroacoustics (ESA9800, Matec Applied Sciences), respectively. The results indicate that the isoelectric point (IEP) is at a pH of 3.5 and 10.5 for the 10-3 vol% and 1 vol% solid suspensions, respectively. Paik and Hackly provide an explanation for the complex surface potential of BaTiO3 particles in aqueous suspension. They attribute this behavior to hydrolysis, i.e., a barium depleted reaction layer forms on the individual particle surfaces whose thickness depends on the equilibrium concentration of dissolved Ba2+ in the aqueous medium. A thick reaction layer with an IEP at pH 4.5±0.5 forms on the surface of individual BaTiO3 particles at low solids loading and low pH. This reaction layer is difficult to distinguish from TiO2, which has an IEP at pH 3.5 and may coexist on the surface. At high solids loading and high pH, however, the surface of the individual particles are Ba2+ rich and have an IEP at pH 10.5.

Hydrolysis effects are generally observed in aqueous, barium-based perovskite suspensions, including the Ba0.98Ce0.8Y0.2O3-x and Ba0.98Ce0.6Y0.2Zr0.2O3-x systems of interest for hydrogen separation membranes. Zeta potential measurements were carried out as a function of pH for dilute Ba0.98Ce0.8Y0.2O3-x and Ba0.98Ce0.6Y0.2Zr0.2O3-x suspensions (10-3 vol%) using capillary electrophoresis. The isoelectric point (IEP) of these systems is at a pH value of ~ 4.5±0.5, indicative of a thick, Ba2+ depleted reaction layer. Furthermore, a characteristic pH value of 9.5 is observed for both the Ba0.98Ce0.8Y0.2O3-x and Ba0.98Ce0.6Y0.2Zr0.2O3-x systems where a sharp decline in zeta potential occurs. This pH correlates with the IEP of doped CeO2, suggesting the coexistence of CeO2 on the surface.

Interparticle forces govern the rheological behavior of colloidal suspensions and must be optimized to obtain slightly shear-thinning flow at high solids loading. Long-range, attractive van der Waals forces are ubiquitous and must be balanced by one or more repulsive forces to optimize suspension behavior. Homopolymer polyelectrolyte dispersants, e.g., poly(acrylic acid) and poly(methacryic acid), are commonly used to impart repulsive electrosteric interparticle forces. However, multivalent counterions, i.e., Ba2+, concentrate the aqueous solution phase of Ba0.98Ce0.8Y0.2O3-x and Ba0.98Ce0.6Y0.2Zr0.2O3-x based suspensions and render these dispersants useless. To solve these problems, a novel dispersant based on a comb-polymer architecture was implemented. This dispersant has an ionizable, poly(acrylic acid) (PAA) backbone (pKa = 5.5) and charge neutral, poly(ethylene oxide) (PEO) teeth grafted onto the backbone at frequent intervals. The PAA backbone serves to anchor the dispersant onto the oppositely charged particles and the PEO teeth ensure that repulsive steric forces imparted by the comb polymer are insensitive to the presence of multivalent counterions in the solution phase. Suspensions of Ba0.98Ce0.8Y0.2O3-x and Ba0.98Ce0.6Y0.2Zr0.2O3-x with solids loading as high as 45 vol% were formed with the aid of the comb polymer dispersant. After a few hours of mixing, these suspensions exhibited shear-thinning flow behavior suitable for a dip-coated process, although further development will be required to optimize slurry composition.

One drawback of the current formulation is that the suspensions stiffen irreversibly with age, which we attribute to the precipitation of BaCO3. This phenomenon is known to occur in BaTiO3 suspensions if the Ba2+ and CO32- concentration in solution, which increases with hydrolysis and mixing with the surrounding atmosphere, respectively, exceeds the limit of BaCO3 solubility (Ksp =2.6¥10-9). To prevent these aging effects, we intend to passivate the surface of the Ba0.98Ce0.8Y0.2O3-x and Ba0.98Ce0.6Y0.2Zr0.2O3-x particles using oxalic or phosphoric acid. Surface passivation will prevent hydrolysis, thus keeping the dissolved Ba2+ concentration, and ultimately, the precipitation of BaCO3 to a minimum.

ISSUES

None

Report Prepared By	Date
T. Armstrong	01/28/04