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Freeze-Cast YSZ Pore Networks: Effects of Alcohol Additives

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Abstract

Freeze casting yttria-stabilized zirconia (YSZ) can be useful in making electrodes for solid oxide fuel cells (SOFCs) by introducing hierarchical porosity to increase triple phase boundary (TPB) area while maintaining adequate fuel flow. In this study the influence of alcohol additives on pore structure of aqueous YSZ freeze-cast samples was investigated. Slurries with ethanol, iso-propyl alcohol, or methanol as additives were compared to a control sample. Pore characteristics along sample lengths were measured using X-ray computed tomography reconstructions. The control sample showed significant changes in pore size along sample length, whereas pore size of the alcohol additive samples remained similar, indicating that freezing rates of the additive samples remained constant during solidification. Ice lens formation and interactions between alcohols and

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slurry functional additives (dispersant, surfactant, and binder) resulted in complex pore structures which show promise in increasing SOFC TPB area.

1. Introduction

Directional freeze casting is a well-known method of making porous ceramics for use in a variety of applications such as filters, thermal insulators, and energy devices.¹⁻³ Pores within the freeze-cast structures are negative copies of the solidified liquid within the slurry, meaning characteristics of the pore network such as porosity, pore size and shape, surface area, and tortuosity are highly dependent on the type of liquid, or dispersion medium, and freezing conditions used.⁴ For example, changing the dispersion medium from water to camphene to tert-butyl alcohol changes the pore morphology from lamellar to dendritic to prismatic, respectively.⁵ Pore size can be altered as well, achieving smaller pores as freezing velocity increases.^{3,4} Freeze-cast pore structures can further be altered through the use of additives in the dispersion medium. Cryoprotector additives and antifreeze proteins decrease the freezing point of water and are used to alter ice growth kinetics and change the structure of the ice crystals themselves, resulting in different pore shapes when used in freeze casting.⁶⁻⁸ For example, numerous studies observed smaller pores and increased connectivity between walls in ceramic samples cast from aqueous slurries with glycerol.⁹⁻¹¹ The hydrogen bonds that form between water and glycerol inhibit complete ice crystallization, limiting ice crystal size and decreasing resulting pore size. Addition of glycerol also reduced volumetric expansion of water upon solidification, likely increasing the amount of micro-porosity within the ceramic walls that were removed during sintering to give denser ceramic walls.¹⁰

Only a few freeze casting studies have explored the use of alcohols such as ethanol, tert-butyl alcohol (TBA), or isopropyl alcohol (IPA) as additives and their effects on pore network characteristics. Munch *et al.* used 4 wt.% ethanol in aqueous alumina slurries and saw a bimodal pore width distribution in the lamellar structures and the appearance of “pocket-like dendrites” on the lamellae surfaces.¹² The authors also noted that lamellar wavelength of the sample with ethanol added was larger for a given freezing time compared to their control sample, as well as samples with other additives (trehalose, sucrose, and NaCl). Porter *et al.* investigated the influence of IPA on the pore structure in freeze-cast titania and concluded that including IPA resulted in elongated ice crystals, perpendicular to the direction of ice growth, with finer surface features (though similar lamellar wavelengths), and decreased mechanical properties compared to samples without IPA.¹³ Zeng *et al.* examined the effect of ethanol and 1-propanol on slurry viscosity and compressive strength of alumina samples.¹⁴ Addition of these alcohols showed increased slurry viscosities, inhibiting the expulsion of ceramic particles from ice crystals, increasing resistance to ice growth, and ultimately decreasing lamellar wavelength. They concluded that compressive strength was improved because of the increased connectivity between ceramic lamellae from the addition of alcohols, and noted that alcohol additives also resulted in denser ceramic walls. Finally, Guizard *et al.*, concluded that inclusion of TBA in aqueous yttria-stabilized zirconia (YSZ) slurries resulted in hierarchical porosity in structures not strictly lamellar in morphology.¹⁵ The authors attributed these observations to the formation of TBA-water eutectic upon slurry solidification, their choice of alcohol concentration being the eutectic concentration.

The current study investigates the effects of three different alcohol additives in YSZ slurries intended for use in solid oxide fuel or electrolysis cells (SOFC, SOEC, respectively) like those produced by researchers at the NASA Glenn Research Center (NASA GRC) using freeze-tape-casting.¹⁶⁻¹⁸ The NASA SOFC design uses freeze-tape-casting as a way to get directionally graded and interconnected porosity.¹⁷ NASA's bi-supported design, prior to nickel and lanthanum strontium ferrite (LSF) infiltration, consists of a stack of porous YSZ electrodes separated by dense YSZ electrolytes, shown in Figure 1. Pore size of the freeze-cast tapes increases as freezing progresses vertically; small pores are beneficial for increasing triple-phase boundary (TPB) area and larger pores are better for gas transport.¹⁶ The freeze-tape-casting method also increases pore alignment along the tape pulling direction, to decrease fuel and air back pressure. The NASA design takes advantage of the naturally occurring protrusions on the ceramic walls in freeze-cast structures, which form due to the formation of ice dendrites; such protrusions may increase TPB area without significantly hindering gas flow.^{19,20}

The goal of this study was to explore the effects of alcohol additives on the pore structure of freeze-cast YSZ samples, evaluating the suitability of the alcohols for use in making freeze-tape-cast SOFC stacks. Samples were made using a stationary casting setup to better determine the natural effects of the additives on the pore structure. Ethanol, IPA, and methanol were investigated to examine how chemistry may influence the resulting pore network characteristics.

2. Experimental Methods

Solids loading for all alcohol additive samples was 25 vol.% YSZ (manufacturer reported median particle size of ~700 nm, Sigma-Aldrich, Saint Louis, MO, USA) with Darvan C-N ammonium polymethacrylate anionic dispersant (Vanderbilt Minerals, LLC, Norwalk, CT, USA) and Dynol 604 ethoxylated acetylenic diol surfactant (Air Products, Allentown, PA, USA). The compositions of the liquid dispersion media with alcohol additives as well as the reported freezing temperature of water within solution are listed in Table 1. The amounts of alcohol additives were chosen so slurries had similar freezing point depressions.²¹ A control slurry was also made with no alcohol additives.

After initial ball milling of the above slurries for 24 hours, Duramax binders were added to enhance both strength and flexibility. The inclusion and amount of functional additives used (dispersant, surfactant, and binders) were chosen to emulate the compositions used at the NASA GRC for freeze-tape-casting of YSZ, comparable to those published by Sofie.²² Solids loading after addition of the surfactant, dispersant, and binders was approximately 15.2 vol.%. Slurries were milled slowly for two additional hours before casting in a simplified setup on a large, methanol-chilled cold surface at the NASA GRC. Approximately 15 mL of each slurry was cast in a Mylar[®]-lined PVC pipe ~3.5 cm inner diameter with ~0.5 cm thick walls and no surrounding insulation. Slurry was poured into the mold from room temperature, placed on the cold plate that was methanol-chilled to -25°C (±2°C) and allowed to freeze completely. Approximate freezing times were between ~17 and 23 minutes and were similar for all samples. Samples were transferred to a pre-chilled freeze dryer after solidification was complete and dried for 24 to 48 hours under reduced pressure. After drying, samples were sintered at 1450°C using the schedule shown schematically in Figure 2. Post-sintered sample heights were between 8 and 10 mm.

Samples were analyzed using scanning electron microscopy (SEM), X-ray computed tomography (XCT), and Archimedes' density method. SEM images were obtained using a Hitachi S-3400N-II SEM (Hitachi High Technologies America, Inc., Pleasanton, CA, USA) and a JEOL JSM-840A SEM (JEOL USA, Inc., Peabody, MA, USA) at the NASA GRC. Methods of extracting XCT samples were presented previously.⁴ XCT was performed at the Advanced Photon Source at Argonne National Laboratory.²³ The control sample was scanned at beamline 2-BM-A using 60 keV white beam X-rays, a 2x lens, a 60 mm working distance, a combination of filters including 15 mm of silicon and 50 mm of glass microscope slides, and a 100 μm LuAG:Ce scintillator. The CCD field of view was 3300 x 1600 pixels and 1500 projections were recorded over 180° using a Pointgray GS3-U3-91S6M-C camera with a 50 ms exposure time. The detector size was $(3.7 \mu\text{m})^2$ and the resulting voxel size was $(1.85 \mu\text{m})^3$. The alcohol-additive samples were scanned with a 7.5x Mitutoyo long working distance lens at a working distance of 50 mm. A CCD pco.dimax CMOS camera recorded projections 2016 x 1700 pixels and the resulting pixel size was $(1.47 \mu\text{m})^3$. The detector physical pixel size was $(11 \mu\text{m})^2$. Samples were scanned at two or three locations along sample height. Using physical measurements and voxel size, reconstructed images corresponding to specific locations were identified.

Datasets were reconstructed using TomoPy, an open source tomographic data reconstruction package, and image stacks were segmented using algorithms built into ImageJ (National Institutes of Health), followed by cleaning in MATLAB[®].^{24,25} Images and image stacks were analyzed in 2D and 3D in MATLAB[®] using methods described previously and modified versions of those methods for porosity, pore size, geometric specific surface area (GSA, defined as the surface area of pores per unit bulk volume), and tortuosity.^{4,26} Porosity and pore size were measured in 2D using slices along sample height. Porosity was calculated using a built-in function and pore size was obtained using the skeletonization–Euclidean distance mapping technique described previously with an added branch trimming step.⁴ GSA was calculated in 3D on stacks using a marching cubes method.^{27,28} Tortuosity was measured along the freezing direction along a three-dimensional skeletal mesh, which ultimately defined the pore network, using the path length ratio technique.²⁸⁻³⁰ Choosing a random set of nodes at the top and bottom of the 3D stack that were connected, tortuosity is reported as the 50th percentile of the set of measurements.

Porosity and apparent specific gravity of porous samples were measured using the Archimedes' density method described in ASTM C373.^{31,32} Water was vacuum-infiltrated into the samples, altered from the boiling method described in ASTM C373 because moderately fragile samples tended to flake during boiling, increasing uncertainty in measurements. Previous studies of more robust samples indicated that this change in process did not significantly alter the measurement results.³³

3. Results and Discussion

3.1. Microstructural Characterization

Figure 3 shows SEM micrographs of the top surface of each sample. All samples exhibited lamellar porosity but the alcohol additive samples, Figure 3(b), (c), and (d), had a variety of surface features and protrusions that were not observed in the control sample, Figure 3(a). Figure 4 shows XCT cross-sections of the control sample and the alcohol additive samples at several locations along sample heights. All samples show primarily lamellar pores, a result of the aqueous chemistry of the

slurries. Pore size of the alcohol additive samples observed in Figure 4 appear similar along sample length, especially compared to the difference in pore size between images of the middle and top regions of the control sample, Figure 4(e) and Figure 4(a), respectively.

Cross-sections of the control sample show lamellar pores many of which are in well-aligned domains. There are few ceramic bridges or protrusions between the pores. Intersecting domains produce non-lamellar ceramic walls, which are observed in all samples but are typically smaller in the control sample compared to the alcohol additive samples. The ethanol sample, Figure 4(b), (f), and (i), exhibits a range of intra-pore features – ceramic bridges and walls forming smaller, secondary pores between the larger lamellae – examples of which are indicated by the arrows in Figure 4(f) and can be seen in Figure 3(b). XCT cross-sections for the IPA sample, Figure 4(c) and (g), show that this sample has fewer intra-pore features than the other alcohol additive samples which may have resulted from pore elongation perpendicular to the freezing direction, a phenomena previously observed by Porter *et al.* for a water-IPA system.¹³ The IPA sample XCT images also show a high number density of non-lamellar ceramic walls resulting from intersecting domains compared to the other alcohols. The methanol sample in particular, Figure 4(d), (h), and (j), has large domains of ordered porosity. There are also, however, areas of very small, aligned lamellar pores in the methanol sample, much smaller than the surrounding pores, observable in Figure 3(d) and indicated by the box in Figure 4(h). Ceramic bridges spanning the distance between two walls or protruding into the pore space are abundant in the alcohol additive samples whereas the control sample has much smoother walls. Bridges in samples made without alcohol additives are believed to be a result of dendrites growing from the primary lamellar ice crystal or dendrite tip splitting and healing, described by Deville *et al.*³⁴ Studies of the effects of glycerol on freeze-cast ceramics have concluded that increased connectivity between ceramic walls is a result of molecular interactions between glycerol and water which disrupt crystallization and reduce ice crystal size.^{7,9-11} The ceramic bridges that formed in the alcohol additive samples in this study, however, are different from those observed in glycerol studies. The cause of these differences is discussed further in Section 3.3.

Table 2 is a summary of porosity and apparent skeletal density from Archimedes' measurements. Apparent skeletal density measurements provide an indication of the amount of closed porosity that exists in each sample adopting the reasonable assumption of good infiltration of open porosity by water; lower apparent skeletal density infers more closed porosity within the ceramic walls. Results for apparent skeletal density show that the amount of closed porosity is highest in the control sample and lowest in the methanol sample, despite all samples having identical solids loading.

Also of note is the relative mechanical strength of the samples. The control sample, which has the highest measured porosity, was quite fragile, flaking from the sides when touched. In contrast, the ethanol and IPA samples were very robust and required a blade to be cut. Porosity and percent apparent skeletal density values can explain these trends; lower porosity combined with higher percent apparent skeletal density results in better mechanical properties, a relationship seen in all freeze casting studies, but also observed by Zeng *et al.* in their studies of ethanol and IPA additives in freeze-cast alumina.^{14,35} The abundance of ceramic bridges between adjacent pores also likely increased the mechanical properties of the additive samples studied here.

3.2. Pore Network Analysis

Figure 5, Figure 6, and Figure 7 show measurements of porosity, pore size – a combination of pore width, wall width, and lamellar wavelength – and GSA, respectively, from XCT cross-sections along sample height. Comparing Figure 5 to Table 2, XCT porosity measurements exhibit the same trends observed from the Archimedes' results. Differences between the measurement methods are likely due to the limited resolution of the XCT images.

XCT measurements show that pore sizes of the additive samples are relatively constant along the freezing direction, with the exception of the methanol sample where lamellar wavelength remained approximately constant over all but the top ~3 mm of the sample. The known inverse relationship between pore size and freezing front velocity suggests that constant pore size in the alcohol additive samples resulted from constant freezing front velocity. In contrast, lamellar wavelength in the control sample increases by over 40 μm or ~130% along sample height. GSA measurements of the control sample show a significant decrease along sample height, inversely related to the trends in pore size, as has been well established.^{4, 26} In contrast, alcohol additive samples show no significant changes in GSA through the thickness.

Given that pore size is inversely related to freezing front velocity, one can infer that the freezing velocity of the additive samples quickly reached a steady state from initial instants, and progressed at about the same rate along the majority of the sample lengths.³ Conversely for the control sample, pore size started small and increased, indicating that freezing front velocity slowed down as freezing progressed, a typical result for porous freeze-cast samples made using the quenching method on a pre-chilled cold surface.^{26, 36} For the additive-alcohol systems, larger pores are reasonably assumed to originate from slower freezing front velocity, despite identical freezing surface temperatures. This change in velocity is believed to stem from limited diffusivity of molecules and mobility of ceramic particles due to higher viscosity of the slurry, a result of addition of alcohols and interactions between alcohols and functional additives, and discussed in detail in Section 3.3.^{26, 36, 37} The challenge that remains is determining why freezing front velocity would reach a steady state and remain approximately constant over sample length for the alcohol additive samples versus the decrease in velocity both expected and observed in the control sample. One hypothesis relies on studies that have examined the influence of glycerol on freeze-cast ceramics and describe how glycerol impedes solute and ceramic particle rejection during formation of ice crystals and limits diffusion of water molecules to crystals to hinder ice growth.⁹⁻¹¹ Zeng *et al.* made similar conclusions for ethanol and IPA additives.¹⁴ It is hypothesized for the current study that constant and slower freezing front velocities are a result of the competition between molecule diffusion and crystal growth, the rate-limiting process being diffusion. If heat extraction were the rate-limiting process, freezing front velocity would decrease as freezing progressed and the amount of material between the cold surface and the solid-liquid interface increases. Instead, if the rate of heat removal via the freezing surface is faster than the rate at which ice crystals can grow from limited molecule diffusion, the freezing rate would remain approximately constant.

Minimum, 50th percentile (median), and maximum tortuosity measurements of the middle regions of each sample are listed in Table 3. Tortuosity was measured along the freezing direction and remained similar across all samples except for the methanol sample, which had much higher median tortuosity. Increased tortuosity may result from increased number density of ceramic bridges or a higher degree of misalignment between adjacent lamellae. Considering that the IPA

sample qualitatively has the highest degree of non-aligned lamellae among the alcohol additive samples, it is likely that increased tortuosity of the methanol sample was due to the multitude of secondary pores that formed bridges instead of disordered and non-parallel lamellar pores. Both ethanol and methanol have a significant number of ceramic bridges that resulted from dendritic growth or secondary lens formation. However, the variance in tortuosity values between the two samples, with the methanol sample having a tortuosity more than double that of the ethanol sample (at the 50th percentile), suggests that there may be differences in the number density of these bridges.

3.3. Alcohol–Additive Interactions

Alcohol concentrations were chosen such that water within the solutions would freeze at similar temperatures, listed in Table 1. Phase diagrams of each alcohol with water are shown in Figure 8, with colored dotted lines indicating the slurry concentrations and casting temperature of the freezing surface used in this study.^{38, 39} The ethanol and IPA phase diagrams include several ice clathrate hydrates that vary in structure and stability based on temperature and concentration of alcohol.^{38, 39} Clathrate hydrates (or hydrates) are crystalline water-based solids resembling ice with small molecules trapped inside “cages” of hydrogen-bonded, frozen water molecules.^{40, 41} More significant than the formation of these hydrates is that for the casting surface temperature used in this study (−25°C), all the water-alcohol solutions are still in an area of the phase diagrams where the only phases present are pure-water hexagonal ice and an alcohol-rich aqueous liquid. This liquid solution, however, also includes the ceramic particles and functional additives and thus is likely high in viscosity.¹³ Studies have also shown that addition of alcohols (ethanol and IPA) or glycerol to aqueous slurries also increases viscosity.^{10, 14}

Despite that the liquid in the slurries were at a higher temperature than the equilibrium freezing temperature of the solution according to the phase diagrams, upon visual inspection the slurries appeared to freeze completely and did not melt or deform during demolding. The contrast between the water–alcohol phase diagrams and the observations made in the current study suggest that other interactions occurred to make the slurries behave as though they were completely frozen. One possibility is that the alcohols evaporated. Slurry recipes were such that each sample cast from approximately 10 mL of slurry included only about 1 mL (or ~0.8 g) of alcohol. However, a room-temperature test using IPA found that evaporation is too slow to fully explain the observed behavior of the water–alcohol mixtures, especially considering the lowered temperature of the slurry during casting. Alternatively, the alcohols could have interacted or reacted with the functional additives, i.e., the dispersant, surfactant, or binders. Individual combinations of each alcohol and each functional additive were blended to determine if any interactions take place between the additives and the alcohols. Results are shown in Figure 9 and described in Table 4. At least one functional additive interacts with the alcohol for each sample type, forming a highly viscous liquid or gel, the viscosity of which is likely to increase as temperature decreases. A second test was run to observe the interaction between the binder Duramax B1000 and the other two functional additives alone (not shown). In both cases a highly viscous gel formed, with little to no fluidity, like the gels that formed between the functional and alcohol additives. In the slurries for freeze casting, no reactions between the alcohols and additives or binders were observed prior to solidification. However, as freezing proceeded and water was continually removed from the solution via ice formation, the concentration of alcohol in the slurry solution increased. The functional additives or binders within

the liquid slurry could then interact with the alcohols, more closely mimicking the direct interactions between functional and alcohol additives observed in Figure 9. The result of this combination of interactions could be an apparent solidification due to the formation of gels that remove alcohol from the system and help samples maintain their structure upon de-molding. Within the freeze dryer any alcohol or water in the gels that formed would evaporate or sublime, leaving behind the polymer solids from the gels which would act as binders and subsequently be removed during the binder burnout stages of sintering. Thus, it is believed that interactions between alcohols and additives had a significant impact on the complexity of the pore structures and may be the primary cause of secondary pore and ceramic bridge formation.

Regarding the use of alcohols in freeze-tape-cast YSZ electrodes for SOFCs and SOECs to increase performance, two assessments can be made. Graded porosity is desired for increasing TPB area through smaller pores near the electrolyte while decreasing resistance to gas flow in the larger pores further from the electrode-electrolyte interface. The negligible difference in pore size of alcohol additive samples between the sample tops and bottoms may not provide the desired graded porosity. The large number density of ceramic bridges and secondary pores within the alcohol samples believed to result from interactions between alcohols, particularly methanol, may be extremely beneficial in increasing TPB area, but, especially within the methanol sample which had increased tortuosity along the freezing direction, they may hinder gas flow compared to the pore structure of the control sample.²⁰ Other methods of increasing TPB area without significantly increasing tortuosity include incorporating a second sacrificial phase or by partial sintering to achieve submicron porosity, as it is not achievable in freeze-cast structures.^{37,43} Alternatively, SOFCs can be improved by modifying the electrode pore surface through infiltration of particles.⁴⁴ Studies by Chen, *et al.*, have demonstrated that freeze-tape-casting of nickel-gadolinium-doped ceria can be used to produce hierarchically porous cathodes with low tortuosity that, when infiltrated with SSC ($\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$) particles, have high cell power output.^{45,46} Computer simulations of freeze-cast ceramic structures indicate that addition of such particles can significantly increase TPB density without sacrificing the advantageous low tortuosity associated with a lamellar pore structure.⁴⁷ It is hypothesized that increasing cell performance by infiltration of a second phase could be applied to the structures in this study given similar tortuosity values to the aforementioned studies and known high permeability of lamellar structures.⁴⁸

The next step in determining the applicability of alcohol additives for use in SOFCs and SOECs is to test the influence of multi-directional freezing induced by freeze-tape-casting, where pores are not only aligned vertically along the freezing direction but also have increased alignment along the tape pulling direction.²² Such alignment may reduce any increases in tortuosity due to the ceramic bridges, enough so to justify higher TPB area caused by the bridges.

4. Conclusions

The use of alcohol additives in aqueous YSZ slurries resulted in highly complex pore structures with many ceramic bridges and domains of disordered, non-parallel lamellar pores. The phase diagrams for water–alcohol binary mixtures indicate that complete solidification would not occur at the casting surface temperatures, instead forming two phases, one of solid ice and the other an alcohol-rich aqueous solution. However, increased viscosity of the slurry at low temperatures and interactions between alcohols and the functional additives may have allowed the samples appear frozen while maintaining structural integrity of the sample prior to sintering. Porosity of alcohol

additive samples was lower than that of the control sample but the alcohol samples had denser walls, resulting in qualitatively higher mechanical integrity. Observed macro-scale pore sizes of alcohol additive samples were larger than that of the control sample when examining XCT cross-sections along the entire sample lengths, but measured pore sizes reflected the presence of ceramic bridges between the larger ceramic walls. Pore sizes of the alcohol additive samples did not vary as much as the control sample over the course of freezing. These results indicate that the freezing front velocity of the alcohol samples was lower than that of the control sample and remained approximately constant over the majority of the sample length. The plethora of intra-pore features in the alcohol additive samples increased maximum pore network tortuosity; the methanol sample had the highest tortuosity. Use of the alcohols explored in this study in freeze-tape-cast YSZ for use in SOFCs and SOECs holds promise for increasing TPB area, and thus performance, due to the large number of secondary pores and ceramic bridges within the primary, lamellar pores.

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List of Figure and Table Captions

Figure 1: SEM image showing a unit cell of an SOFC/SOEC stack design by NASA using freeze-tape-cast YSZ electrodes.

Table 1: Amount of alcohol additives and reported freezing temperatures of the water – alcohol solutions.²⁰

Figure 2: Schematic of the sintering schedule utilized.

Figure 3: SEM images of samples with (a) no additives, (b) 20 vol.% ethanol, (c) 20 vol.% IPA, and (d) 12.3 vol.% methanol.

Figure 4: XCT cross-sections from the base to the top for the four samples. A base region scan could not be performed on the control and IPA samples. Pores = dark, ceramic walls = white. Scale bar = 200 μm .

Table 2: Summary of Archimedes' density measurements.

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Table 3: Minimum, 50th percentile, and maximum tortuosity measurements for the middle region of each sample.

Figure 8: Phase diagrams of water with ethanol, IPA, and methanol. Colored dotted lines indicate compositions of alcohol slurries (orange) and cold surface temperature (blue). L = liquid, ice = pure frozen water, α = ethanol_(s), β = IPA_(s), γ = CH₃OH·H₂O_(s), h_1 = type I hydrate, h_2 = type II hydrate. Black dash lines indicate metastability of hydrates. Some monotectic transitions and hydrate formations are omitted from the IPA diagram for clarity. Adapted from Murthy, Aladko *et al.*, and Dougherty.^{37, 38, 41}

Figure 9: Interactions between functional additives and alcohols.

Table 4: Results of interactions between the functional additives and the alcohol additives.

Table 1: Amount of alcohol additives and reported freezing temperatures of the water – alcohol solutions.²⁰

Slurry	Additive Amount	Freezing Point Depression
Water + Ethanol	20 vol.% (7.2 mol.%)	-8.3°C
Water + IPA	20 vol.% (5.6 mol.%)	-6.6°C
Water + Methanol	12.3 vol.% (5.9 mol.%)	-6.6°C

Table 2: Summary of Archimedes' density measurements.

Sample	Porosity (%)	Apparent Skeletal Density (%)
Control	62.6	93.4
Ethanol	50.5	95.3
IPA	52.9	95.6
Methanol	57.7	96.3

Table 3: Minimum, 50th percentile, and maximum tortuosity measurements for the middle region of each sample.

Sample	Tortuosity		
	Min	50th %	Max
Control	1.01	1.03	1.13
Ethanol	1.00	1.03	1.72
IPA	1.00	1.02	1.82
Methanol	1.02	2.37	2.86

Table 4: Results of interactions between the functional additives and the alcohol additives.

	Dynol 604 (Surfactant)	Darvan C-N (Dispersant)	Duramax B1000/B1022 (Binders)
No alcohol	Liquid only	Liquid only	Liquid only
Ethanol	Liquid only	Viscous liquid (honey-like)	Mostly liquid
IPA	Liquid only	Viscous liquid (honey-like)	Mixture of solid masses in liquid
Methanol	Liquid only	Highly viscous liquid (gel-like)	Liquid only









