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Understanding Binary Interactions and Aging Effects in Catalyst Layer Inks for Controlled Manufacturing

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The effect of perfluorosulfonated ionomer loading in carbon-based colloidal inks is investigated under static and dynamic operating conditions. The results show that both the solvent-type and polymer loading play a role in ink stability, aggregation, and aging. Dynamic light scattering and shear and creep rheological experiments show that the addition of a polymer to carbon inks can act as a stabilizing agent which increases steric repulsion and decreases the inks overall viscosity. As the polymer loading is increased above 30wt% a decrease of approximately 30 MPa^{-1} in compliance is observed. A decrease in compliance at high polymer loading suggests weak interactions between the underlying carbon materials and indicates that a critical polymer loadings may exist for different shear processing routes.

Introduction

Catalyst layers in polymer electrolyte fuel cell applications are typically manufactured via solution-processed approaches where the active material and binder are dispersed in a multi-component ink. Different properties can be obtained depending on the formulation of the ink and the manufacturing approach (i.e. spray coating, doctor blade, decal transfer). The arrangement of the key materials (catalyst, carbon, and ionomer) and the overall microstructure of the catalyst layer is important for effective mass transport and high active material utilization (1). The ability to control microstructural properties via controlled ink design or engineered processes has not yet been fully achieved, but is critical for scalable manufacturing of membrane electrode assemblies (2).

Previous investigations have suggested that the proton conducting binder used in fuel cell catalyst layers (perfluorosulfonic acid) does not form a true solution in most solvents but instead forms a colloid (1-3). The structure of this colloid can take on different morphologies which in turn can affect the mechanical durability, coatability, and component microstructure. Furthermore, results suggest that the solvent plays a critical both in the formation and mitigation of agglomerates (2,4-5) within the ink phase as well as the mobility of the polymer in the solvent (2). The multi-component and multiphase nature of catalyst layer inks is governed by numerous interactions (polymer|solvent, solvent|polymer, particle|polymer) that are nearly impossible to probe through any single technique. Herein, we specifically aim to eliminate some of the heterogeneous nature of these ‘ink’ systems and systematically evaluate the effect of the solvent and polymer loading on properties governing the coatability of carbon-based inks. We use both static (dynamic light scattering) and transient (rheology) techniques to probe properties relevant to understand the shelf-life (aging) and processing of inks for catalyst layers.

Materials and Methods

Materials and Ink Preparation

All solvents (Table 1) used in this study were analytical grade reagents sourced from Fisher Scientific and the active material used in all inks was Vulcan carbon XC-72. The ionomer suspension used was a 5 wt.% nafion dispersion sourced from Fuel Cell Store. The typical ink formulation procedure is as follows: Inks were prepared in small glass vials by mixing appropriate amounts of carbon with the solvent [10 gm Solvent, 0.1 wt.% Carbon]. The mixture was probe sonicated for 20 minutes (1 minutes on, 1 minute off) to break up the aggregates and homogenize the suspension.

$$W_{ionomer} = \frac{m_{ionomer}}{m_{ionomer} + m_{carbon}} x100$$

For ionomer containing inks, the ionomer amount needed for each loading is calculated using the above equation. Here $W_{ionomer}$ is the weight % of the ionomer needed. For this study 15%, 30% and 50% ionomer contents as prescribed by the above equation were studied. The ink preparation method will be similar to that described above, however the ionomer dispersions were added prior to sonicating.

Table I. Solvents proposed to be used in this study with key physical properties

Solvent	**Viscosity [cP]**	**Dielectric Constant [-]**	**Surface Tension [N/m]**
Glycerol	1412	42	6.30E-2
1-Octanol	7.363	10.2	2.75E-2
Isopropyl Alcohol	2.04	19.92	2.17E-2
Water	1	80.1	7.28E-2
Methanol	0.56	32.7	2.22E-2

Ink Stability

The as-prepared inks were allowed to sit and images were taken at regular intervals to study the sedimentation process.

Rheology

The rheological studies were carried out on a DHR 3 Rheometer (TA Instruments, USA) with a concentric cylinder assembly (bob diameter: 28 mm, cup diameter: 30.4 mm, gap 5917.1 μm). Only the methanol inks are evaluated for these studies. The shear sweeps were run at ambient temperature for all inks. To ensure that no shear history is present in the sample, the samples are pre-sheared at 100 s^{-1} for 15 s and allowed to rest for 15 minutes prior to each run. The shear sweeps are run from 3700 s^{-1} to 1 s^{-1}. The linear amplitude sweeps were run between 0.01% and 10% amplitude strain. From the identified strain value from these runs, the oscillatory sweeps were run between 0.1 to 600 rad/s. Further, to understand the time dependent behavior of the inks, creep experiments were carried out at a constant stress value of 0.01 Pa for 3600 s.

Dynamic Light Scattering

DLS measurements were carried out on Malvern Nano-ZS zetasizer. The DLS measurements were carried out on undiluted inks. The physical properties of the solvents used are listed in Table 1. The refractive index of carbon is taken as 2.41. All samples were run twice, with each sample run consisting of 15-20 individual scans. The average values along with standard variations are reported

Results and Discussion

Particle Aggregation in Inks

Colloidal stability is defined as the ability for an ink or dispersion to resists aggregation and sedimentation processes. For electrochemical systems it is important to avoid aggregation during processing in order to achieve uniform and control microstructures. Dynamic light scattering was used to study the effect of solvent and polymer loading on the stability of as-prepared and aged carbon-based inks. The particle size results for bare carbon inks show an increasing trend as glycerol > water > isopropyl alcohol > methanol > octanol (Fig. 1). For bare inks, the primary sizing will be governed by hydrodynamic forces acting on the carbon particles in the inks. Glycerol has higher surface tension [6.3E-2 N/m] that results in decreased particle sizes. Water [7.28E-2 N/m], and IPA [IPA: 2.17E-2 N/m] have dissimilar surface tension properties but similar dielectric constants, viscosities, and aggregation properties (Fig. 1a). The other two solvents have comparable surface tensions [MeOH: 2.22E-2, Octanol:2.75 N/m] and demonstrate the largest aggregation sizes between 600-800nm.

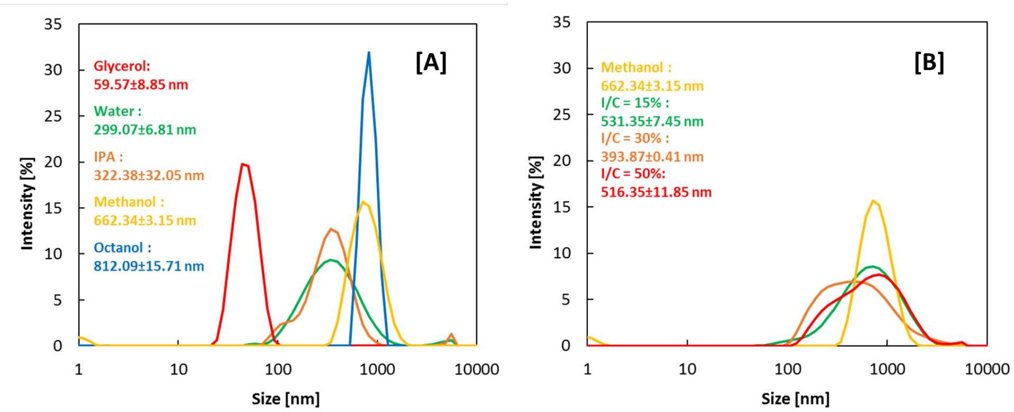
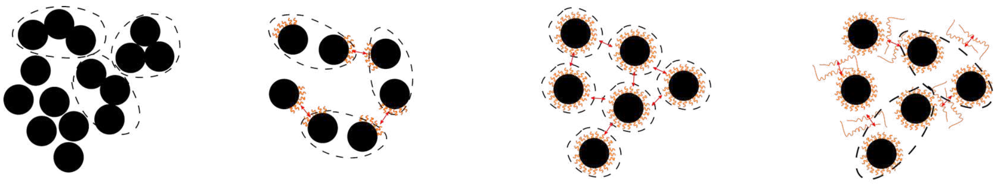


Figure 1. DLS studies for bare carbon [A] and ionomer containing inks (solvent: methanol) [B]. The average particle size and the standard deviations are shown in the figures.

The effect of ionomer content of aggregate size on methanol inks is shown in Fig. 1B.. A slight reduction in aggregation size is observed as the polymer is increased from 0wt% to 15 and 30wt%, but above 30wt% the particle size distribution is similar to the bare carbon ink. A control study with IPA at the same concentrations showed no variation with ionomer content. However, a control ink study with higher carbon loading and corresponding ionomer content showed a marked increase in aggregate size. The increase in particle size at high carbon content loading can be described by a great surface area for ionomer adsorption. However, restricting the discussion to low carbon loaded inks, the following description can be used to describe the effect of polymer loading on aggregation dynamics:

- No Ionomer Content: Particle aggregation governed by hydrodynamic and electrostatic forces [d_{avg} = 662.34±3.15 nm]
- Low Ionomer Content: Partial surface coverage; some steric repulsion; breaking up of previous aggregates; decrease in particle size [d_{avg} = 531.35±7.45 nm]
- Medium Ionomer Content: Full surface coverage; significant steric repulsion; isolation of aggregates; decrease in particle size [d_{avg} = 393.87±0.41 nm]
- High Ionomer Content: Excess ionomer in ink; possible secondary aggregation of isolated aggregates; increase in particle size [d_{avg} = 516.35±11.85 nm]

A non-linear trend exists between polymer loading and aggregation behavior. Furthermore, an increased polydispersity index is seen for all the ionomer containing inks as compared to the bare carbon ink. This could possible suggest a uniform ionomer penetration through the inks. A graphical figure of the polymer-carbon interaction is presented as **Figure 2**..



Zero I/C:
Bare Caron in Solvent
Size governed by solvent effects

Low I/C:
Lower surface coverage
Steric repulsion leading to particle seggregation
Decreased Particle Size

Medium I/C:
Optimum surface coverage
Decreased Particle Size

High I/C:
Unattached polymer leading to secondary aggregation
Increased Particle Size

Figure 2. Phenomenological representation on effect of ionomer addition to the aggregate sizes. Carbon particles are depicted by black spheres, ionomer chains by orange lines, while proposed aggregates are depicted by dashed lines. An optimum of polymer concentrations is observed in terms of minimum aggregate size. The red arrows depict the steric repulsion acting between the polymer chains

Ink Stability and Aging

A visual analysis of sedimentation was performed to describe aging effects for bare carbon inks and carbon/polymer inks. Fig. 3 demonstrates that the methanol and octanol inks are unstable. The former sediments after an hour, while the latter settles between 30-43 hours. The instability of methanol inks have been previously reported. The differences between the different solvents can potentially be attributed to decreasing electrostatic repulsion as is perceived by their dielectric constants [MeOH > IPA > Octanol]. Furthermore, it should be noted that methanol inks are highly unstable and this is observed from the dynamic light scattering results. The average particle size fluctuates and polydisperisty index (P.D.I) increases over time:

- T≈ 10 min; d_{avg}= 662.34±3.15; P.D.I = 0.29
- T≈ 40 min; d_{avg}= = 3240.44±132.10; P.D.I = 0.34
- T≈ 24 hr; d_{avg}= 857.22±149.31; P.D.I = 0.79

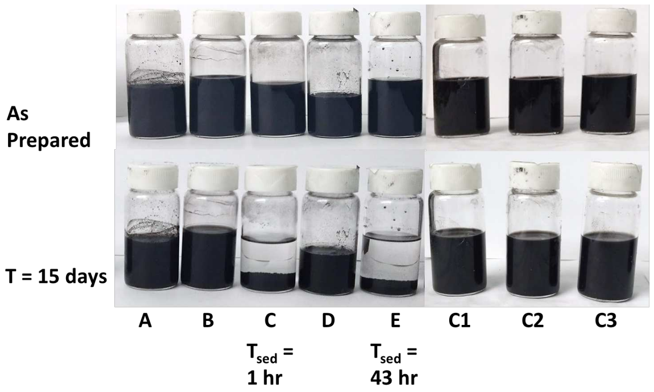


Figure 3. Visual stability analysis. The solvents are A: water, B: isopropyl alcohol, C: methanol, D: glycerol, E: octanol. The C1, C2, C3 inks are ionomer containing inks with methanol solvent and I/C ratios of 15, 30 and 50% respectively. The sedimentation times for two inks is mentioned in the figure as T_{sed}

The addition of an ionomer to the methanol inks has a pronounced effect on improving the stability of the inks. The ionomer containing inks are found to be stable even after 15 days. The DLS of aged methanol inks demonstrated a reduction of aggregate size for all the inks independent of polymer loading (Fig. 4). The aged inks converge to a uniform aggregation size of [<280 nm] suggesting the limited effect of polymer loading on aggregation of bare-carbon polymer inks. Furthermore, these results demonstrate favorable implications of ink ageing in terms of decreasing aggregation size.

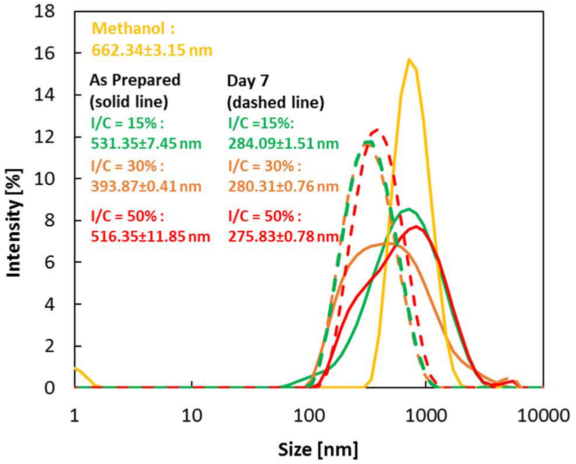


Figure 4. DLS studies for aged methanol inks. The average particle size and the standard deviations are shown in the figures.

Shear-Induced Effects in Inks (Rheology)

Only methanol inks were studied via rheology as an indirect tool to understand the effect of polymer addition on the stability of the inks (Fig. 5). All inks show a shear thickening behavior where the hydrodynamic forces overcome the structuring forces provided by the layered flow developed in the interim shear range. All the ionomer inks show a decreased viscosity compared to the bare carbon ink due to an added steric repulsion by the addition of the ionomer. The ionomer reduces the restoring force provided by the adjacent fluid layers, thereby reducing the effective viscosity (Fig. 5A). Only the storage moduli have been reproduced for oscillation sweep and oscillatory sweep studies. The loss moduli represent the viscous component of a viscoelastic response. Since all the inks have the same solvent (methanol) which forms the majority of the suspension, they are seen to be identical for all the inks studied.

However, marked variation in storage moduli are seen. At low amplitude the storage of inks containing 15 and 30% ionomer, have lower storage moduli compared to the bare carbon inks. Lower storage moduli implies that the material is less likely to relieve the applied strain. This is possibly due to the fact that polymer is not confined and yields easily compared to carbon. Above a critical concentration, the polymer cannot yield and dissipate the applied strain and hence the storage modulus rises from 30-50%. This is consistent with the earlier phenomenological model which proposed that at high ionomer concentration, excess ionomer is present in the dispersion. A similar explanation can be construed for the results seen in oscillatory sweep experiments. Further, the tailing off of the storage moduli suggests that the inks are chiefly viscous gels.

To understand the time dependent behavior of methanol inks creep studies were carried out. The compliance curves of bare carbon ink and ink with 50% ionomer overlap completely. The compliance increases from bare carbon to 30%, before falling back for 50%. Compliance is defined as the strain per unit stress applied to the material. As ionomer concentration increases, we see a decreased storage modulus signifying the ability of the material to yield at lower stress values. This increases from 30 to 50% as the concentration becomes high enough that it is not possible for ionomer to dissipate the applied stress. At this concentration, the ionomers reconfigure themselves in the matrix without transferring the energy to another ionomers, thereby effectively ’storing’ the applied stress, increasing the storage modulus.

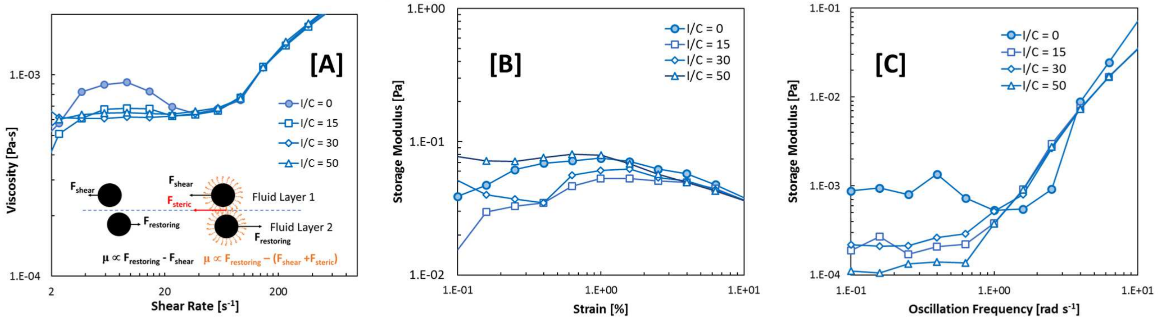


Figure 5. Rheological studies of methanol inks. Samples pre-sheared at 100 s-1 for 15 s and allowed to rest for 15 minutes prior to each run. [A] Steady shear sweeps [B] Amplitude sweep, and [C] oscillatory sweeps.

Conclusions

We present a systematic and multi-scale approach to understanding catalyst layer inks under static (shelf) and dynamic (processing) conditions. To decrease the heterogenous nature of a catalyst we explore a model system composed of bare carbon and PFSA in a range of solvents. The results demonstrate that PFSA acts as a stabilizing agent in unstable solvents (methanol and octanol) but has limited impact on the aggregation of the solid particles within an ink. Across all solvents studied, aging seems to favorably reduce the aggregation size. While polymer loading has limited impact on the aggregation size in an ink, it has a significant impact on the flowability which will in turn be of importance during processing. The compliance of an ink initially increases with the addition of a polymer, but decreases significantly above a critical threshold (polymer loading).

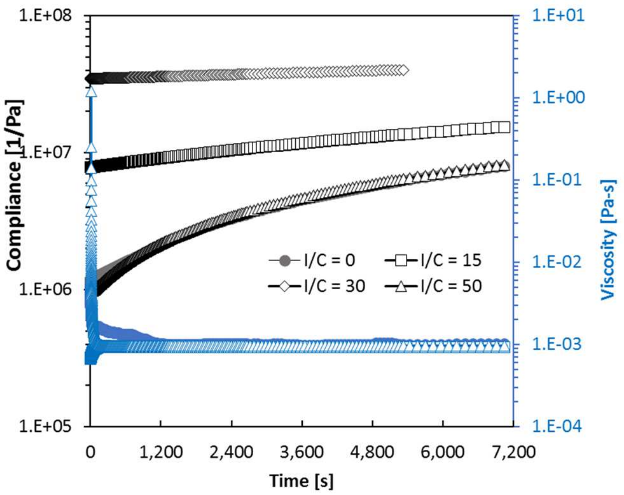


Figure 6. Creep studies for methanol inks with varying I/C ratios.

Acknowledgments

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