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Carbomer – Zinc interaction: rheological detection of polymer adsorption onto metallic microparticles

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The objective of this work is to develop a polymer gel capable of stabilizing zinc microparticles for redox flow batteries. This is challenging since such system is characterized not only by high density particles ; but also by a high alkaline media inherent of the redox flow battery^{1,2}.

To test the properties of the proposed PAA network, zinc suspensions in PAA gels are prepared at controlled pH conditions with the purpose of identifying microscopic interactions that can be detected by the macroscopic rheological behaviour of PAA gels. PAA gel is first studied alone to determine the effect that polymer concentration and pH can have on its rheological behaviour. In fact, let's underline that yield stress is a key parameter of a percolated network and for the prevention of sedimentation in suspensions. Next, the effect of the addition of zinc particles to the gel is studied with the objective to characterise zinc-PAA interactions. For this purpose, zinc suspensions of different PAA and zinc particle concentrations are prepared and then centrifuged. Our hypothesis is that PAA and zinc will bound after formulation and hence, centrifugation will make zinc particles settle together with the potentially bound PAA polymer. If some of the PAA is indeed bound to zinc particles, a polymer-depleted supernatant will be recovered after centrifugation, and its polymer concentration will therefore be lower than the initial polymer concentration of the suspension. Hence, zinc-PAA interactions will lead to a polymer concentration decrease in supernatant.

To evaluate this hypothesis, the concentration of polymer in the supernatant was determined. The first approach consists in a rheometric method that we will refer to as “inverse rheometry”. This method will allow to calculate PAA concentration from supernatant rheological properties accordingly to its physicochemical properties, especially its pH. A second qualitative approach consists in labelling the polymer using rhodamine dye, and then quantifying the gel adsorption using light absorption. Finally, the bulk-effect of the gel adsorbed onto zinc particles is discussed in regard to its suspending capacity.

Our results confirm the presence of zinc-PAA interactions indicating that an interconnected percolated network³ in an alkaline media can be built using PAA polymer, in which PAA will not only transport ionic species crucial for the cell reaction in redox flow batteries, but also effectively suspend zinc particles avoiding sedimentation.

This study also shows that rheometry can be an accessible and powerful tool to determine interactions when compared to other direct, but less accessible methods, based on light adsorption.

It was also emphasized in this work that not only physicochemical sample properties, as pH, can affect the yield stress and thus the gelled network. Indeed, the presence of ionic species in solution and possible particle-gel interaction can also affect the gel yield stress, by modifying the physicochemical suspension properties, and consequently, its macroscopic behaviour.

¹ Mainar AR, Iruin E, Colmenares LC, et al. Journal of Energy Storage 2018.

² Nelson AZ, Ewoldt RH Soft Matter 2017

³ Bernkop-Schnürch A, Krajicek ME Journal of Controlled Release 1998