AGGREGATION OF IONOMER AND CARBON BLACKS
DURING MEA PREPARATION:
MODEL TO CHARACTERIZE PARTICLE SIZE
AND CATALYST ACCESSIBILITY

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Aggregates form when ionomers such as Nafion are mixed with small particles. The formation of these aggregates is driven by particle surface area and cohesive energy between ionomer fluorocarbon side chains. A model is suggested for relating the size of aggregates to basic properties of the ionomer and particles. The model is applied to inks of Nafion and the platinized carbon black, Vulcan XC-72. Design notions for varying the properties of MEA inks are presented.

INTRODUCTION

Membrane electrode assemblies (MEAs) for proton exchange membrane (PEM) fuel cells are variously formed by coating inks of polymer and catalyzed carbon black against the outer surfaces of the membrane separator. Typically, the assembly is then heat treated. Using a mixture of polymer and carbon black to form the catalyst layer or interface was first reported by Raistrick (1) in 1986. Polytetrafluorethylene was a commonly used, but it has been largely replaced by ionomers such as Nafion® and Flemion®.

The ionomer in the catalyst layer can serve any of several purposes. Ionomer can increase ionic conduction in the interface; serve as a binding agent for the components in the interface; and help control wetting.

Here, it is suggested that the ionomer also controls the size of the catalyst aggregates in the interface. Experimental results are presented for composites of Nafion and nanostructured materials that illustrate effects of molecular packing and aggregate formation. A model that correlates the size of ionomer/carbon black aggregates with the molecular dimensions of the ionomer and the radius of the carbon black particles is presented. From the model, suggestions are made for controlling the size of carbon black aggregates in the catalyst layer based on ionomer structure and particle size.
EXPERIMENTAL SECTION

Composites were formed by sorption of Nafion onto and into model, nanostructured materials (2–6). Neutron track etched polycarbonate membranes (CoStar, Nuclepore) are 6 μm thick, and traversed by co-linear cylindrical pores. Each membrane contains a single diameter pore, and had pore densities of the order of 10^6 pores/cm^2. Pore diameters of 15, 30, 50, and 100 nm were used (2,3) in Nafion/neutron track etched membrane composites. In Nafion/microsphere composites, polystyrene microbeads (Polyscience) with diameters of 0.11, 0.22, 0.37, and 1.1 μm were used (4,6).

Composite Formation

Nafion/neutron track etched composites were formed by soaking the membranes in Nafion suspension (5% wt/vol Nafion in alcohol/water - Solution Technologies) for 30 minutes. Upon removing the membranes from the soaking solution, the exterior surface was briefly blotted to remove excess suspension adhering to the outer surface of the membrane. The composites were dried overnight in a vacuum desiccator.

Nafion/microsphere composites were formed by cocasting appropriate volumes of Nafion suspension (Aldrich) and microsphere suspension (2.5% wt/vol in water). Casting solvents were allowed to evaporate and the composites were placed in a vacuum desiccator for one hour. Composites contained 50% microbeads by volume, and were approximately 10 μm thick. The density of the microspheres was reported by the manufacturer as 1.05 g/cm^3. The density of the cold cast Nafion was taken as 1.40 g/cm^3, as recently determined (7).

Titration Experiments

The majority of the titration experiments were performed on Nafion/neutron track etched membrane composites. The protocol for these experiments was as follows (3). (1) Weigh the membrane. (2) Soak the membrane in the Nafion suspension, remove excess suspension form the surface of the membrane, and allow the solvents to evaporate. This forms the composite. (3) Soak the dried composite in hydrochloric acid solution to convert the sulfonates to the protonated form. (4) Dry and weigh the composite. (5) Place the composite in 1 M NaCl to flush the protons from the composites, and titrate the protons with NaOH to a phenolphthalein endpoint.

SEM Images

Scanning electron microscopy (SEM) images were taken of the Nafion/microsphere composites by casting the composites on silicon wafers. Micrographs were taken with Hitachi S-2700 and Hitachi S-4000 SEMs. Magnifications of 10× the microbead diameter in each composite were used.
RESULTS

**Titration Experiments for Nafion/Neutron Track Etched Composites**

The titration experiments yield two different assessments of the amount of Nafion in the Nafion/neutron track etched composites. The difference in the weight of membrane and the composite (membrane + Nafion) yields the actual weight of Nafion in the composite. The titration of the composites yields the millimoles of sulfonate groups in the composites that are actually available for ion exchange. The equivalent weight of the Nafion in the suspension was determined by titration to be 1046 grams of Nafion per mole of $SO_3^-$. The surface area of the membranes was known from the pore diameters and the porosity of the membranes. It was found that as the surface area of the membrane increased, the moles of sulfonates found by titration decreased relative to the moles of sulfonates found by weigh. That is, as surface area increased, the moles of sulfonates available for exchange decreased. This is illustrated in Figure 1.

From Figure 1, the fraction of sulfonates available for ion exchange decreases linearly with the surface area over which the Nafion is sorbed. This leads to several observations and conclusions (2).

1. It is the sulfonate groups that interact with the surface that become unavailable for ion exchange.
2. This is consistent with the intercept at zero surface area yielding a value consistent with the 1046 EQWT found for the bulk Nafion material.
3. The slope of the plot yields a cross sectional area per sulfonate unavailable for ion exchange. This cross sectional area has a radius of $0.25\pm0.02\,\text{nm}$
4. This radius is consistent with roughly monolayer coverage of sulfonates over the surface of the polycarbonate.

The cylinders of the composite are packed effectively with Nafion. The interior surface of the pore is coated with a monolayer of Nafion where the sulfonates adsorb to the surface and the fluorocarbon tails point radially into the interior of the pore. The remainder of the pore is filled with bulk Nafion, no different in properties than a simple Nafion film.

**SEM of Nafion/Microsphere Composites**

SEMs of the microsphere composites are shown in Figure 2. It is immediately apparent that the composites formed with microbeads with diameter $\geq 0.22\,\mu\text{m}$ form self similar and well distributed clusters. In the composites formed with the smallest microbeads with diameters of $0.11\,\mu\text{m}$, the beads are not well distributed, and cluster into larger aggregates. The larger aggregates have diameters of 1 to $2\,\mu\text{m}$.
DISCUSSION

Packing Consideration

The results for the Nafion/neutron track etched materials illustrate that if the support structure is large enough, the ionomer can pack effectively into the structure and form a cohesive monolayer. The result also illustrate that the Nafion preferentially adsorbs to the surface as a monolayer and then fills the remainder of the pore with a structure typical of cast Nafion films.

Titration experiments for the smallest pore diameter of 15 nm were not successful because the uncertainties in determining the weight of sorbed Nafion were too large. However, flux results reported elsewhere (2) indicate that the side chains of the Nafion do not pack effectively into a pore of 15 nm because the tails are too crowded to pack well in the interior of the pore.

Molecular Structure of Nafion 1100

\[-(CF_2CF_2)_8 - CF(CF_2)OCF_2CFOCF_2CF_2SO_3H\]

Packing considerations in nanostructured materials have been considered by Halperin, Tirrell, and Lodge (8). They showed that as the characteristic length of nanostructures decreases, the lengths become comparable to the dimensions of the molecules in the system,
and this impacts molecular packing. The specific case here can be appreciated by considering the molecular lengths of Nafion. The molecular structure and lengths of the side chains (1.5 nm) and backbone between side chains (2.5 nm) are shown. Based on density calculations for various linear fluorocarbons, the diameter of the tube formed by the side chains is 0.41 nm.

When two sulfonates adsorb next to each other, the monolayer is formed of a thickness of $1.5\,nm + \frac{2.5\,nm}{2} = 2.75\,nm$ because the backbone will bend at its midpoint to allow monolayer formation. This is illustrated.

![Diagram of monolayer formation](image)

In the 15 nm diameter pore, formation of the monolayer is not possible because cylinder of length 2.75 nm and a diameter of 0.41 nm cannot pack radially and in contact along their lengths inside a circular structure of only 15 nm diameter.

Packing is again a factor in the microsphere composites. For the larger beads, the Nafion can pack effectively along the surface of the beads and sufficiently well into the volumes where two beads touch that each bead is individually wrapped in Nafion. Nafion monolayers can bridge small gaps. As the bead diameter decreases, the fraction of the surface covered by the Nafion decreases because the Nafion cannot pack sufficiently well into the volume where two beads touch, and a different structure is generated. This is illustrated below.

![Diagram of packing](image)
The structure of the microsphere composites is driven by packing and the cohesive energy between fluorocarbon chains. The energy needed to solubilize one $CH_2$ group in water is 2 to 4 KJ/mol (9); it is expected that the energy to solubilize the $CF_2$ groups of Nafion will be significantly higher. Thus, the most favored structure for the Nafion will minimize interactions between the $CF_2$ groups and water while maximizing the interactions between $CF_2$ groups. Such a structure is best provided by forming a Nafion monolayer at the surface of the inert polymer supports of polystyrene microbeads and polycarbonate membranes. In the microsphere composites for the smallest diameter beads, the cohesive energy between fluorocarbon chains is sufficiently high as to gather the smallest microbeads into a larger aggregate. The aggregate provides a better structure over which the Nafion monolayer can form.

To appreciate the impact of poor packing of the monolayer where two beads touch, consider the diagram of two spheres in contact.

Let $r$ be the radius of the microsphere, and $a$ be the thickness of the adsorbed monolayer. For Nafion, $a = 2.75$ nm. The left most point in the diagram corresponds to the place where the tails of two adsorbed ionomer monomers collide, one tail on the top bead and one tail on the bottom bead. This collision sets the limit of how well the ionomer packs into the volume where the two spheres touch. This is reflected in the angle $\theta$, where $\theta$ measures the cap of each sphere where no coating with ionomer is possible. $\theta$ is related to $a$ and $r$ as

$$\theta = \arccos \frac{r}{r + a}$$

(1)

It is clear that as $a$ increases, $\theta$ increases, and less of the surface is coated by ionomer.
For a 0.11 μm diameter bead coated with Nafion, θ is 17.8°. This is for the point where two beads touch and represents a significant fraction of the bead surface not covered by ionomer. In a close packed structure, each bead has several nearest neighbors, and the fraction of uncoated surface will be significant. Because the cohesive energy between fluorocarbon chains is sufficiently high it can overcome the drag resistance of the smallest particles, and sequester them into an aggregate with particles on the interior and ionomer monolayer draped around it. It is not dissimilar to marbles inside a balloon, where the air has been vacuumed out of the balloon.

Model

These observations can be generalized with a model to predict the size of an aggregate based on the thickness of the monolayer formed by the ionomer and the size of the beads or particles used in the composite. The model is directly applicable to the inks used to cast MEA catalyst layers, where the particles are the platinized carbon black particles. The model assumes that formation of a monolayer by the ionomer is the driving force for aggregate formation, and that the particles inside the aggregate are close packed.

Define the following variables.

- Volume of the aggregate - $V_{agg}$
- Volume of a single spherical particle - $V_{part}$
- Radius of the aggregate - $R$
- Radius of the particle - $r$
- Number of particles in the aggregate - $n_{part}$
- Specific surface area of particles - $ssa$ (cm$^2$/g)
- Avogadro number - $N_0$
- Equivalent weight of the ionomer - $EQWT$
- Surface area covered by one chain of the monolayer - $\sigma$ (cm$^2$/chain)
- Weight of particles per cm$^2$ - $w_{t_{part}}$
- Weight of ionomer per cm$^2$ - $w_{t_{ion}}$

Assume the particles inside the aggregate are close packed. Then, the number of particles in an aggregate is

$$n_{part} = \frac{0.76V_{agg}}{V_{part}}$$

$$= 0.76 \left(\frac{R_{agg}}{r_{part}}\right)^3$$

Note that particles inside an aggregate are less effective catalysts because they are shielded from the environment where the reactants and products are mobile.
Let
\[
\alpha = \frac{EQWT \times ssa}{N_0 \times \sigma}
\]  
(4)

Then,
\[
\frac{R_{agg}}{r_{part}} = \frac{\alpha}{0.76} \times \frac{wt_{part}}{wt_{ion}}
\]  
(5)

The size of the aggregate is thus determined by the properties and amount of material in the ink. The amount is embedded in the ration \(wt_{part}/wt_{ion}\). The characteristics of the materials used in the ink is embedded in \(\alpha\), where the properties of the ionomer are its equivalent weight and the cross sectional area of the side chains. For the particles (i.e., carbon black), the specific surface area of the particles is important.

Discussion of Nafion and Vulcan XC-62

The aggregates formed when casting an ink of Nafion as ionomer and Vulcan XC-72 as the platinized carbon black particles are characterized by the above model as follows.

| Table 1: Materials Properties for Nafion and Vulcan XC-72 |
|----------------------------------------------------------|
| **Vulcan XC-72**                                        |
| \(r_{part}\) 1.5 \(\times\) 10^{-6} cm                  |
| \(ssa\) 2 \(\times\) 10^{6} cm^{2}/g                     |
| \(EQWT\) Nafion 1100                                     |
| \(\sigma\) 1.7 \(\times\) 10^{-17} cm^{2}/chain          |
| \(\alpha\) 2.16                                         |

From these parameters, the relationship between \(R_{agg}/r_{part}\) and \(wt_{part}/wt_{ion}\) is shown in Figure 3. The number of particles in an aggregate, \(n_{part}\), is also shown. Note, that as more particles are in an aggregate, the larger the fraction of catalyst buried inside the aggregate, and the less accessible the catalyst will be.

For typical inks used in MEA fabrication, \(wt_{part}/wt_{ion}\) falls in the range between 1 and 10, with values tending to be between 1 and 5. The smaller the ratio of \(wt_{part}/wt_{ion}\), the larger the fraction of catalyst particles on the exterior of the aggregate.

Design Notions for MEA Inks of Ionomer and Carbon Blacks

Several design notions can be extracted from this simple model for changing the characteristics of the catalyst layers produced by forming inks of ionomers and carbon blacks.

- Decreasing aggregate size leaves a larger fraction of the catalyst particles on the exterior of the aggregate, where the particles will be more accessible, and therefore more catalytically active. The size of the aggregates \(R_{agg}\) can be decreased by each of the following.
- decrease $w_{t_{\text{part}}}/w_{t_{\text{ion}}}$
- decrease $r_{\text{part}}$
- decrease $\alpha = \frac{EQWT \times \text{area}}{N_{0} \times \sigma}$

- Forming inks where aggregates do not form would lead to the best dispersion of catalyst as no catalyst particles would be buried inside the aggregates. Small catalyst particles are less likely to form aggregates if the ionomer has the following properties.
  - shorter side chains
  - shorter distances between side chains
  - smaller cross section of the side chains (e.g., hydrocarbon ionomers)

CONCLUSIONS

Aggregates form when ionomers such as Nafion are mixed with small particles. The formation of these aggregates is driven by surface area of the particles and the cohesive energy between the fluorocarbon side chains of the ionomer. A model is developed relating the size of aggregates to basic properties of the ionomer and particles. The model is applied to inks of Nafion and the platinized carbon black, Vulcan XC-72. The properties of MEA inks can be altered by varying $w_{t_{\text{part}}}/w_{t_{\text{ion}}}$, and the properties of the ionomer and carbon black.

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REFERENCES

[1] Raistrick, I. D. in Proceedings of teh Symposium on Diaphragms, Separators, and Ion Exchange Membranes; Zee, J. W. V.; White, R. E.; Kinoshita, K.; Burney, H. S., Eds.; The Electrochemical Society, Inc.: 1986.

[2] Fang, Y.; Leddy, J. J. Phys. Chem. 1995, 99, 6064-6073.

[3] Leddy, J.; Vanderborgh, N. E. J. Electroanal. Chem. 1987, 235, 299-315.

[4] Zook, L. A.; Leddy, J. Diffusion in Fractal Microstructures. in Microstructured and Microfabricated Systems II, Vol. 95-27; Denton, D.; Hesketh, P. J.; Hughes, H., Eds.; The Electrochemical Society, Inc.: 1995.
[5] Zook, L. A.; Amarasinghe, S.; Fang, Y; Leddy, J. *Nano- and Micro-Structured Materials: The Role of the Interfaces in Tailoring Transport*; Vol. II of *Fundamentals of Materials Research Series* Plenum: New York, 1995 pages 355-364.

[6] Zook, L. A.; Leddy, J. *J. Phys. Chem.* 1998, 102,.

[7] Zook, L. A.; Leddy, J. *Anal. Chem.* 1996, 68, 3793-3796.

[8] Halperin, A.; Tirrell, M.; Lodge, T. P. *Tethered Chains in Polymer Microstructures*; Vol. 100 of *Advances in Polymer Science* Springer-Verlag: New York, 1992 pages 31-71.

[9] Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: New York, 2nd ed.; 1992 page 353.
Figure 1: For Nafion/neutron track etched composites, the fraction of sulfonate groups available for ion exchange decreased with the surface area of the membrane.
Figure 2: SEM Images of Nafion/microsphere composites. In each Image, the micron bar is $10 \times$ the microbead diameter.
Figure 3: Variation in aggregate size relative to particle size and number of particles per aggregate \( (n_{\text{bead}}) \) as \( \text{wt Vulcan/ wt Nafton} \) varies in MEA inks. As \( n_{\text{bead}} \) increases, a larger fraction of particles is embedded inside the aggregates where the catalyst is less accessible.