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## Conduction and Mass Transfer in Reinforced Cation Exchange Membranes

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### ABSTRACT

The transport of sodium chloride and calcium chloride through two types of reinforced perfluorinated cation exchange membranes under an electrical field gradient was studied to determine the effect of calcium ion interferences to sodium ion migration. Electromigration-electroosmosis experiments were performed in a diaphragm cell. The concentration of all ions in each half cell was maintained constant by a feedback mechanism. For single salt experiments, the salt flux of calcium ions was half the salt flux for sodium ions. The water flux was higher for the membrane with the greater reinforcement. The effect of two cations competing for migration to the membrane matrix was studied by experiments utilizing a feedback mechanism for each cation. The flux ratio of sodium ions to calcium ions decreased as the concentration of calcium chloride was increased for experiments where the solutions contained mixtures of sodium chloride and calcium chloride.

The electrical conductivity of the membranes was measured using in a diaphragm cell having one movable electrode, allowing for resistance measurements at different path lengths. The resistivity for the membranes in solutions having only one cation was greater for calcium chloride solutions than for sodium chloride solutions. The resistivity of the more reinforced membrane was greater. For a mixture of sodium and calcium ions, as the calcium ion content decreased and the sodium ion concentration was held constant, an increase in resistivity was observed.

The total exchange capacity for the two membranes was measured by soaking samples in solutions containing only one cation or solutions of two cations. With only one cation in solution, the exchange capacity for the membrane having the greater reinforcement was 26 per cent higher than for the other membrane. For solutions containing equal molar concentrations of sodium chloride and calcium chloride, the difference of exchange capacity between the two membranes was 3 per cent.

Adding small amounts of calcium ions to the solution surrounding the membrane had a large effect on the conductance and the ion flux through the membranes. The selectivity of the membrane for sodium ions decreased as the concentration of calcium ions increased.

### INTRODUCTION

Reinforced perfluorinated sulfonate polymer membranes such as the "Nafion" membranes manufactured by E. I. DuPont de Nemours and Company have a high selectivity for cation transport. Some characteristics of these membranes have been described by Grot (1). The membranes are reinforced with polytetrafluoroethylene, and the types intended for use in chlor-alkali production have had the surface treated with ethylene diamine to produce a surface layer having extra cross linking. Two types of "Nafion" membranes were studied--N-417 which has no surface treatment and N-901X which has the surface treatment and which is made especially for chlor-alkali processing.

One objective of the work was to study the transport through the membranes of cations having different charges and to relate the transport to membrane properties and solution concentration. A second objective was to determine the nature of cation transport when two ions having different charges are present and to determine how one cation might interfere with the transport of the other cation through the membrane.

### BACKGROUND

Transport across the membranes was induced by applying an electric field perpendicular to the membrane (2). A diaphragm

cell was used to hold the membranes flat. A "quasi-steady-state" method is frequently used when transport measurements are made in diaphragm cells. All parameters are held constant except for concentration which varies slowly during the course of an experiment. For the work reported here, a true steady-state method was used, and the concentrations of the solutions on either side of the membrane were kept constant for the duration of each experiment. Back diffusion of ions due concentration changes can be eliminated by maintaining a true steady-state situation (3).

The electrical conductivity of membranes has been measured by many authors by comparing the resistance of a system with and without a membrane between two bracketing solutions (4, 5, 6, 7, 8). Others have measured the conductivity by having the membrane in direct contact with mercury, where the membrane had been equilibrated with the same solution as being used for the conductivity measurement (9).

The selectivity of Nafion polymers is known to be similar to the divinylbenzene sulfonate resins (DVB), but some differences do exist. Exchange site clustering is an important factor in determining selectivity properties of Nafion membranes, whereas DVB types have effects from ion exchange capacity, cross-linking, and water sorption (10). Transport through Nafion membranes is usually explained by a diffusional model. Many models have been proposed, but one which is consistent with ionic diffusional results describes diffusion in three different regions of the membrane (11). One region is the fluorocarbon backbone. Another region includes ion clusters containing exchange sites, counter ions, and sorbed water. The third region is composed of a relatively large fractional void volume, which contains side chain materials and smaller amounts of the previously mentioned groups.

### EXPERIMENTAL METHODS

Membrane samples (DuPont N-417 and N-901X) were exercised by alternately immersing in solutions of 2M HCl and 2 M NaCl for 24 hour cycles. The equilibrium properties, exchange capacity, wet weight, water content, and thickness were determined by averaging measurements made for ten samples of each type of membrane. Exchange capacity was measured by regenerating the sample to the  $H^+$  form in 2 M HCl, and then exchanging the  $H^+$  ions by immersing the sample in 2 M NaCl. The resultant solution contained only the previously bound  $H^+$  ions, which were titrated with 0.1 M NaOH. Wet weight was measured in the  $H^+$  and  $Na^+$  forms. To determine the water content, each sample was weighted wet after being immersed in water for at least two weeks. The dry weight was measured after drying the samples in a vacuum dessicator. The water content is expressed as per cent of dry membrane. The thickness in the dry form was measured for ten samples, and the average value was calculated.

The conductivity of the membrane was determined using a conductivity cell (12). The resistance was measured in the cell as a function of the distance between two platinized platinum electrodes of 48.3 mm diameter which can be moved axially in the cell by means of a screw-driven mechanism. Sodium chloride and calcium chloride solutions and solutions containing both ions were used. The resistance was measured at several different electrode separation distances with and without the membrane mounted in the membrane holder. The data from such measurements fell on lines which were straight and parallel. An example is shown in Figure 1. The membrane resistance was calculated from the difference between the two lines. This method has been discussed by Zelman (13). A thermistor probe which was connected to a null detector via a Wheatstone bridge was inserted into the cell body and used for detecting the cell temperature which was maintained at  $25.00 \pm 0.01^\circ C$ .

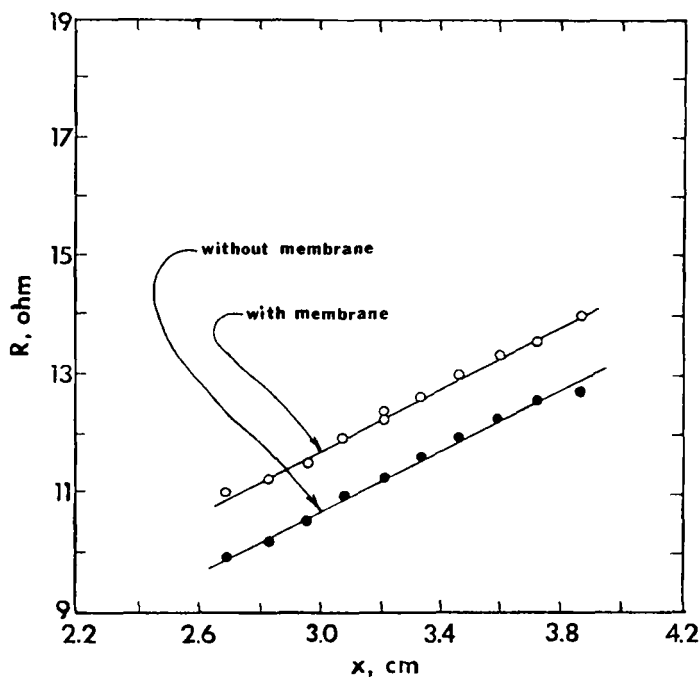


FIGURE 1 Typical membrane resistance data. N-417 membrane, 0.1 M  $\text{CaCl}_2$ , 25.0°C.

Transport measurements with one salt in solution were performed in a "concentration-clamp" diaphragm cell (14). The sources of electrolytic ions were two reversible Ag/AgCl electrodes mounted facing each other at the ends of the cells. Conductivity probes were used as sensors for determining changes in concentration in either half cell. The resistance of the solution was compared to a reference resistor using an impedance comparator. A difference caused a signal which activated a feedback mechanism. An automatic microburet or a closed loop water system injected either a more concentrated salt solution or water to maintain the resistance equal to the reference value. As solutions are injected, liquid comes out through overflow pipets into weighing vessels. From mass balances over each half

cell, the fluxes and transport numbers can be calculated. Cooling coils regulate the temperature in each half cell within  $\pm 0.01^\circ\text{C}$  as detected by two thermistors. To insure well-stirred solutions, each compartment contains a magnetic "Spin-Fin" stirrer rotated by a magnet mounted below the cell.

The fluxes of two competing cations--sodium and calcium--through a membrane were measured in the same "concentration-clamp" cell. The solution of chloride salts in the salt-donating compartment was circulated through an auxiliary reservoir containing specific ion electrodes used as sensors. A difference in potential from the preset limit on a pH controller caused activation of the appropriate salt solution injection mechanism. More concentrated solutions of either sodium or calcium ions were injected into the auxiliary reservoir maintaining a constant concentration of each ion in the salt donating compartment. As described above, liquid is discharged and mass balances are used to calculate the corresponding fluxes and transport numbers. The salt-receiving compartment contains a conductivity probe to sense concentration changes. This activates the dilution system to keep the concentration constant.

### RESULTS AND DISCUSSION

The Nafion 417 membrane is classed as a reinforced durable type. The N-901X membrane is a carboxyl-sulfonate bimembrane and is touted as having high durability, high caustic strength for use in chlorine-caustic cells, high chemical stability, and as having a unique cloth reinforcement made of "Teflon" (15).

The equilibrium properties as measured in this investigation of the DuPont N-901X and N-417 membranes are presented in Table 1. The capacity measured for the N-901X membrane was 26 per cent greater than the N-417 membrane. When the capacity was measured using an equal molar mixture of  $\text{NaCl}$  and  $\text{CaCl}_2$  as the

TABLE 1  
Equilibrium Properties of the Membranes

	N-901X	N-417
Thickness (dry) $10^{-4}$ m	$5.0 \times 10^{-4}$ m	$4.5 \times$
Water Content (dry basis)	13 percent	16 percent
Wet Weight ( $\text{kg/m}^2$ )	0.58	0.66
Exchange Capacity for Single Ions [ $\text{Na}^+$ , $\text{K}^+$ , or $\text{Ca}^{++}$ ] (meq/g dry membrane)	0.97	0.74
Exchange capacity for Two Ions [ $\text{Na}^+$ and $\text{Ca}^{++}$ ] (meq/g dry membrane)	0.62	0.61

exchanging ion the apparent capacity of both membranes becomes the same 0.61 meq  $\text{H}^+$ /gram-dry membrane. The wet weight, water content, and the thickness of the membranes are close to the values of the manufacturer (16). The N-901X membrane had a smaller water content and wet weight and a larger exchange capacity than the N-417 membrane. The lower value obtained for the exchange capacity when both  $\text{Na}^+$  and  $\text{Ca}^{2+}$  ions are in solution is contrary to the expectation for measuring the capacity. A possible reason for detecting fewer exchange sites is that there is an interference affecting the mobility of the ions. If this is true, it could mean that a longer time is required to reach equilibrium when two types of cation are present.

Figure 2 is a plot of the measured conductance versus the external solution concentration. The ranges of experimental uncertainty shown indicate the maximum uncertainty expected for



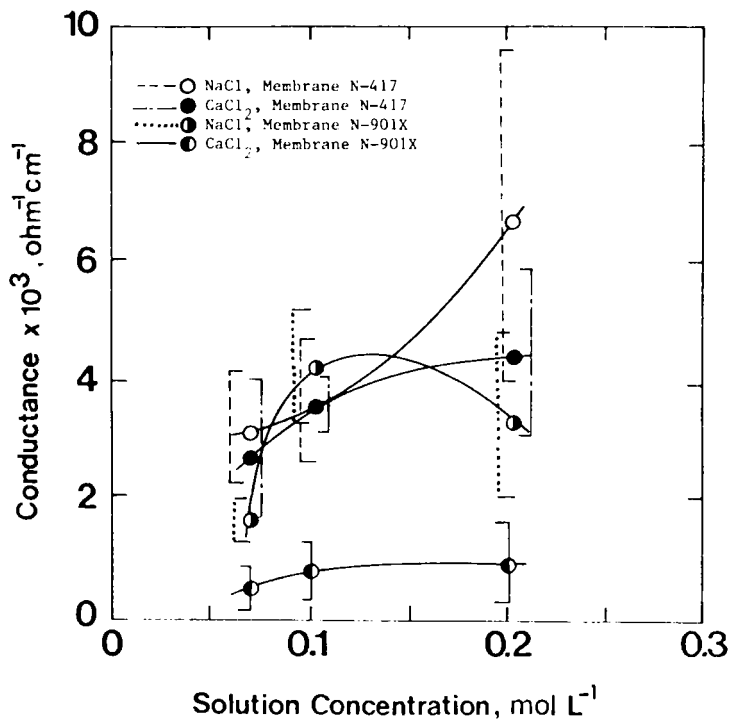


FIGURE 2 Membrane conductance for a single ionic species present.

each calculated value. The lines are drawn to guide the eye and do not represent any fitted correlation. In most cases, the ranges of uncertainty overlap. There is no firm basis for saying that the membrane conductivity for the N-901X membrane depends on the concentration of the solution outside the membrane phase. For the N-417 membrane, there may be some concentration dependence. The concentration dependence seems greater for sodium ions than for calcium ions. The type of ion in the solution influences the membrane conductivity. This is most apparent for the N-901X membrane. The effect increases as the salt concentration increases. For the N-901X membrane, the

conductance was about three times greater for sodium ion solutions than for calcium ion solutions. The conductance for the N-417 membrane was about 1.5 times greater under similar circumstances.

The conductance when the solution surrounding the membrane contains both sodium and calcium ions is shown in Figure 3. Adding one ppm calcium ions to the 0.1 molar sodium chloride solution caused the conductance to decrease to about 30 percent of the value observed with no calcium present. Adding more calcium caused the conductance to increase. At an ionic strength of 0.2 moles--0.1 molar sodium and 0.1 molar calcium--the conductance for the N-901X membrane was about the same as when

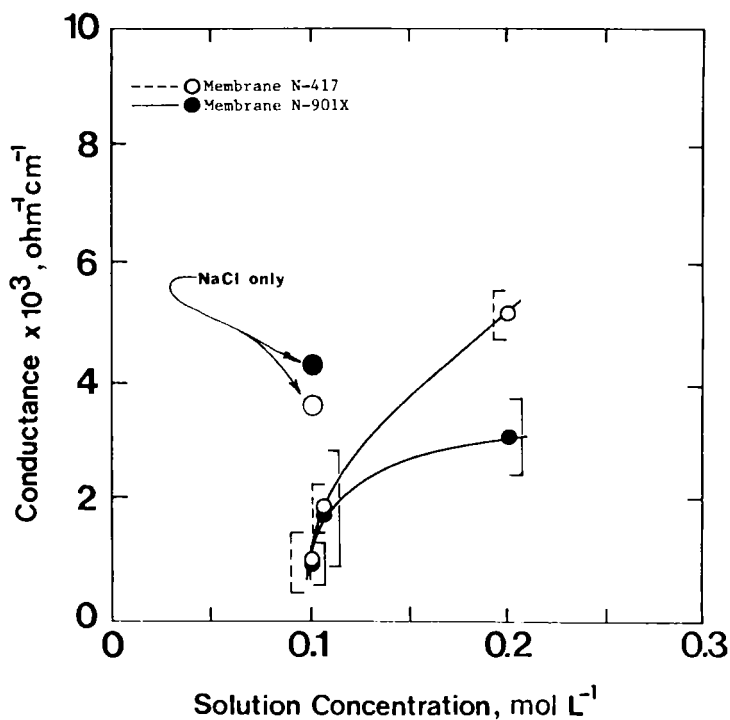


FIGURE 3 Membrane conductance for two ionic species present. 0.1 M NaCl and varying concentrations of  $\text{CaCl}_2$ .

the solution contained 0.2 molar sodium chloride. For the N-417 membrane, the conductance was less than in 0.2 molar sodium chloride solution but greater than in 0.2 molar calcium chloride solution.

All the electro-osmosis experiments were carried out at a current density of  $1 \text{ ma/cm}^2$  with identical solutions on each side of the membrane. An example of the calculated accumulative flux through a membrane is shown in Figure 4. All the lines are fitted through the origin, since at the start of an experiment, there is no material accumulated. The water flux is determined from the difference between two large numbers. This leads to a large uncertainty in these water flux values.

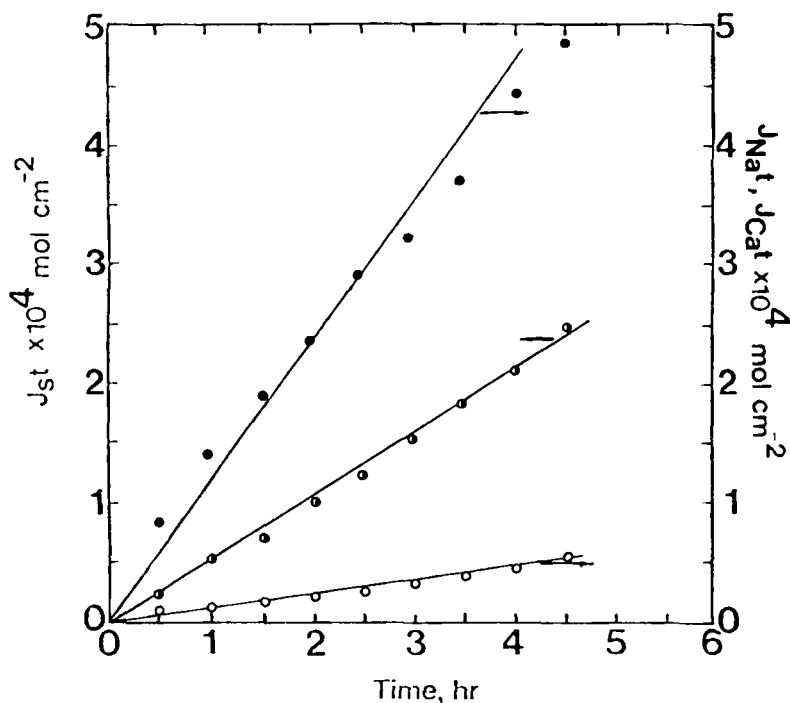


FIGURE 4 Typical ionic flux and water flux data. N-417 membrane 0.1 M NaCl and 0.1 M  $\text{CaCl}_2$ ,  $25.0^\circ\text{C}$ .

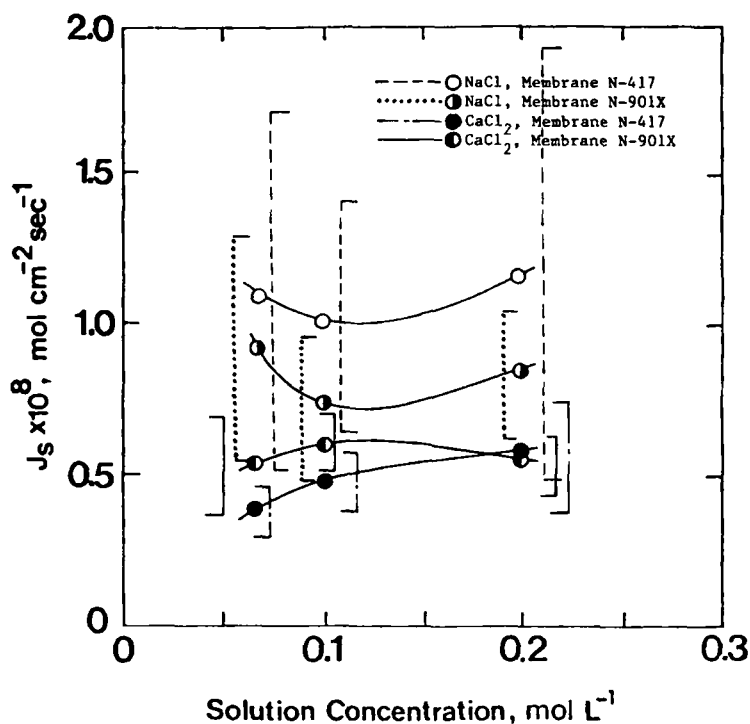


FIGURE 5 Salt flux for a single ionic species present.

A plot of the total salt flux versus the solution concentration is shown in Figure 5 for experiments where only one ion species was in solution. The total salt flux was calculated from an overall mass balance. For the N-417 membrane, solutions with  $\text{CaCl}_2$  show a  $\text{Ca}^{2+}$  ion flux one-half the  $\text{Na}^+$  ion flux. For the N-901X membrane, the ratio is 0.6. As before, the maximum expected uncertainty is indicated in the figure, and again the ranges of uncertainty overlap. There is no real basis for concluding that the fluxes depend on the concentration of the solution surrounding the membrane. This uncertainty makes interpreting the results difficult. One can say that the flux for sodium salts is greater than the flux for calcium salts, but

one notes that comparisons between the two membranes are not clear. For sodium ions, the salt flux for the N-417 membrane is greater than the salt flux for the N-901X membrane. For calcium ions the opposite is apparently true.

Figure 6 shows the ion fluxes as a function concentration when two different ionic species are present in the solution. Sodium chloride concentration was held constant at 0.1 M, and calcium chloride concentration was varied--0.1 M, 0.007 M, and 1 ppm. The concentration axis indicates the total ionic strength of the solution. The calcium ion flux is not zero which means that the membranes are not perfectly selective for sodium. Just as in the case of the conductance, there is a large effect of

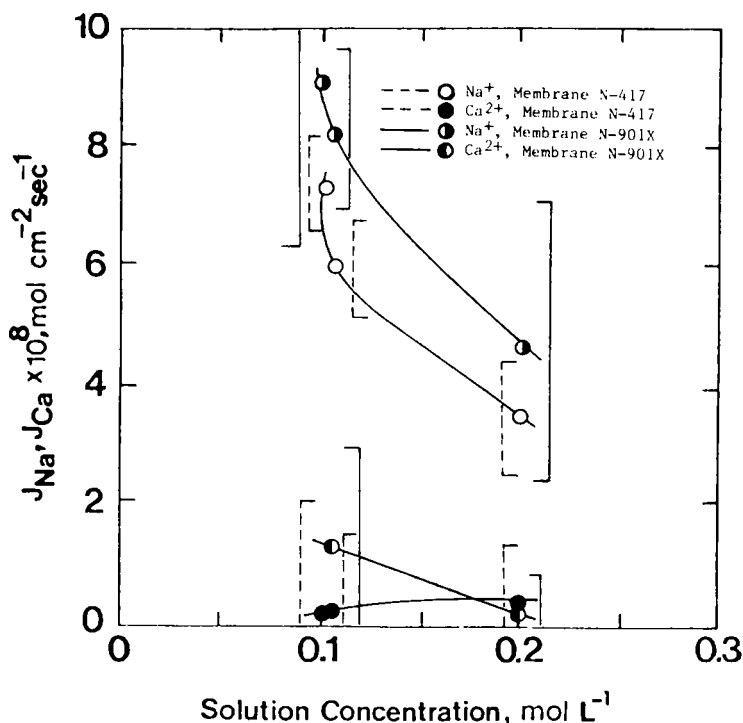


FIGURE 6 Ionic fluxes for two ionic species present. 0.1 M NaCl and varying concentrations of CaCl<sub>2</sub>.

adding calcium ions to the solution. The flux for sodium with even 1 ppm calcium present is four to nine times the flux for sodium ions when no calcium is present. When the calcium ion concentration is increased, the sodium ion flux decreases sharply while the calcium ion flux remains essentially constant. This means that the selectivity of the membranes depends strongly on the concentration of calcium in the solution.

### CONCLUSIONS

The results indicate that small amounts of calcium ions present in the solution surrounding the membrane cause decreases in membrane conductance and increases in sodium ion flux. With increases in calcium ion concentration, the sodium flux is reduced and the conductance is increased indicating some form of interference between the two ionic species. The calcium ions may be more strongly associated than sodium is with the exchange sites in the membrane. This might account for the decrease of sodium flux with increasing calcium ion concentration, but it does not account for the enhancement of sodium flux when very small amounts of calcium are present. The size of the hydrated cations could also be important in the transport of competing ions through the membranes. Complete information about the sizes of the hydrated cations relative the size of the space near the cation exchange sites in the membrane is needed in order to draw conclusions about the mechanism of the interference between the sodium and calcium ions. The nature of the surface treatment of the membrane could play a role in the mechanism of interreaction between two ionic species being transported through a membrane. The selectivity of the membranes depends on the concentrations of the ions in the solution. Others (17) have reported that calcium ions are transported through ion exchange membranes preferentially compared to sodium ions. This is not supported by the present work.

### NOMENCLATURE

- $J_{Ca}$  - Calcium ion flux  
 $J_{Na}$  - Sodium ion flux  
 $J_s$  - Total salt flux  
 $J_w$  - Water flux  
 $R$  - Resistance  
 $t$  - Time from the start of an experiment  
 $x$  - Position coordinate for resistance measurements

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