APPLIED PHYSICS LETTERS VOLUME 77, NUMBER 13 25 SEPTEMBER 2000

Sol-gel coated glass cells for spin-exchange polarized ^{3}He

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(Received 20 April 2000; accepted for publication 28 July 2000)

We have developed a high-purity sol-gel coating for the interior surface of glass cells used for polarizing ^{3}He by spin-exchange optical pumping. The coating is designed to minimize spin relaxation due to wall collisions. A longitudinal spin-relaxation time T_1 in a sol-gel coated Pyrex cell of 344 ± 8 h was achieved, the longest T_1 we have ever recorded for a gaseous sample. Repeated trials indicated that the coating was quite robust. Results using an uncoated Pyrex cell were also quite good, although inferior to the performance of the coated cell. © *2000 American Institute of Physics.* [S0003-6951(00)02839-4]

Noble gases whose nuclei have been polarized by spin exchange with laser-optically pumped alkali-metal vapors have been increasingly employed in fields ranging from medical imaging to polarized nuclear targets.[1] The noble gases are typically polarized in glass vessels, and minimizing spin relaxation due to collisions with the vessel's walls is key to obtaining high polarizations. For the case of ^{3}He, Newbury *et al.* showed that dipole–dipole interactions during collisions between ^{3}He atoms cause the spins to relax at a rate of $1/744\,\mathrm{h}^{-1}$ at a density of one amagat.[2,3] Ideally, one would like to consistently produce cells in which relaxation due to wall collisions is negligible compared to dipole–dipole relaxation.

In this letter, we describe the use of a sol-gel coating[4] as a means for producing glass vessels in which spin relaxation of ^{3}He due to wall collisions is suppressed. We speculate that the suppression is due to carefully controlling the composition of the coating and keeping it relatively free of paramagnetic impurities in comparison to commercial glass. Our best results were achieved using a Pyrex cell whose interior surface was coated with a high-purity aluminosilicate sol-gel film. This cell proved extremely robust over repeated trials and ultimately exhibited a spin-relaxation time somewhat in excess of the longest time that the authors could find in the literature for any gaseous sample.[5] When working with ^{3}He, we have historically used aluminosilicate glasses almost exclusively, a choice determined by the need for resistance to alkali attack and numerous reports, beginning with Ref. 5, that aluminosilicate glasses have good spin-relaxation properties. Unfortunately, aluminosilicate glasses are notoriously difficult to work. Our results using a coated Pyrex cell suggest the possibility of avoiding working with aluminosilicate glasses for many applications. Even when experimental constraints dictate the use of aluminosilicate glasses, the sol-gel coating technique may provide better reproducibility in performance.

Our studies were performed on four sealed glass cells, roughly spherical in shape and approximately 2.5 cm in diameter, designated A, B, C, and D. In preparation for filling, the coated cells were attached to a glass manifold, evacuated, and baked at 400 °C for several days. Also attached to the glass manifold was a side arm containing an ampule of rubidium (Rb). During the bakeout, the Rb was distilled into a small reservoir toward the end of the glass manifold, after which the side arm was ''pulled'' from the system by fusing a glass constriction with a gas torch. At the conclusion of the bakeout, a gas torch was used to chase Rb into the cells, after which they were filled with about 75 Torr of N_2, 2–11 amagats of ^{3}He, and sealed. In order to maintain a pressure below one atmosphere during sealing, cryogens such as liquid N_2 or liquid He were used to cool the cell during the filling process. All gases were passed through chemical getters to remove any impurities before entering the cells.

The cells were coated prior to being sealed to the glass manifold. Two coating compositions were tried, containing molar fractions of alumina of approximately 20% and 50%, respectively. The preparation of the coating solution began by dissolving aluminum nitrate nonahydrate[6] [$Al(NO_3)_3 9H_2O$], in ethanol. We used 9.2 g (23.1 g) of $Al(NO_3)_3 9H_2O$ and 66.9 ml ethanol for the 20% (50%) alumina solutions. For the 20% alumina solution, 6.0 ml of de-ionized water was also used. These solutions were stirred overnight to ensure that the aluminum nitrate was fully dissolved. Next, while still stirring, 11.0 ml (6.9 ml) of tetraethoxysilane[7] was added drop by drop using a disposable plastic pipet. Finally, before coating any cells, the concentrated solution was diluted 7:1 with ethanol and stirred for several days. The coating process proceeded by filling each cell with coating solution, waiting about 2 h, and then emptying it of excess solution. The cells were dried at 60 °C overnight, and placed in a furnace to sinter (densify) the coating. The furnace temperature was ramped up at 300 °C per hour, and held at 550 °C (20% alumina) or 500 °C (50% alumina) for 2 h before turning off power to the furnace. While at high temperature, the coating, which is initially rather porous, densifies by viscous deformation. The result-

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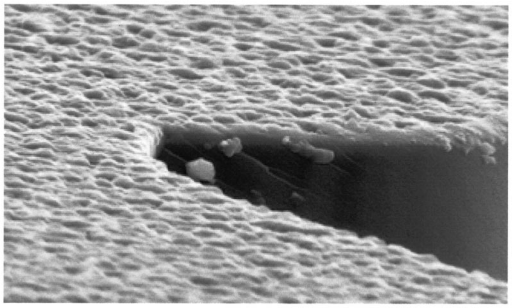

FIG. 1. Shown is a scanning electron microscope image of a sol-gel coating made in a similar manner to the coatings of the studied cells. For scale, the horizontal field of view is about 4.5 μ.

TABLE I. Room temperature measurements, in hours, of T_1 for cells A and B (coated aluminosilicate), cell C (coated Pyrex), and cell D (uncoated Pyrex).

Trial No.	Cell A	Cell B	Cell C	Cell D
1	50±6	22±3	225±41	166±16
2	51±6	20±2	299±56	189±23
3	23±3	23±3	197±23	200±19
4	24±3	20±2	225±30	190±21
5	22±3	18±2	321±67	196±25
6	22±3		361±72	195±22
7			307±51	183±15
8			344±8	241±6

ing coating, an example of which is shown in Fig. 1, is approximately 200 nm in thickness.

To study the robustness of the cells under operating conditions, we performed 5–8 trials on each cell. A trial comprised a ''spin-up,'' during which the ^{3}He was polarized by spin-exchange optical pumping, and a ''spin-down,'' during which the ^{3}He was allowed to depolarize. During the spin-up, the cell was heated to $\sim 180\,°\mathrm{C}$ while being irradiated with 795 nm radiation from high power diode laser arrays. During the spin-down, the cells were at room temperature. Polarization was monitored using a low field ($\sim 15\,\mathrm{G}$) pulse nuclear magnetic resonance (NMR) system. Each time a NMR measurement was made, a single pulse of radio frequency (rf) was sent to the sample, resulting in a free induction decay (FID) which had roughly the shape of an exponentially damped sinusoid. Our magnetic field was not actively locked, so the frequency of the FID, which was the difference between the ^{3}He Larmor frequency and the frequency of the drive rf, drifted slightly with time. For each polarization measurement, we would apply several pulses to the sample, and make small adjustments to the drive rf in order to obtain an FID frequency of about 9 Hz. The polarization was assumed to be proportional to the difference between the first maximum and the first minimum of the FID. The polarization data were fit to an exponential, the time constant of which we quote as T_1. The data from our longest spin-down are shown in Fig. 2.

In the course of our measurements, we noticed that the transverse relaxation time T_2^* of our FID depended on the degree of polarization of our sample. At high polarization, T_2^* was on the order of several seconds, whereas at lower polarizations, it was about 1 s. We determined that this was due to what might be called subthreshold masing, in which the spins couple energy into the NMR pick-up coil.[8] Under these conditions, the loss of polarization resulting from each rf pulse varied from roughly 0.5%–1.7%. When we reversed the direction of the ^{3}He polarization with respect to the magnetic field, the T_2^* was 100–200 ms, independent of the polarization, and the polarization loss per pulse was roughly 0.2%. The raw data from cells C and D were corrected for these effects before being fit to an exponential. The corrections, and associated uncertainties, were largest for trials 1–7 during which the cells were polarized in the masing state. Data from cells A and B were not corrected because these data were taken before we noticed the masing. Trials 1–7 of cells C and D also had larger errors because the spin-downs were only 60–72 h in length, much shorter than the T_1 of either cell. Whereas longer spin-downs would have been desirable, we wanted to study the cells over multiple trials, and as it was, we collected over 2132 h of data. The spin-downs for trial No. 8 of cells C and D were conducted in the non-masing state, and lasted over 600 h and 206 h, respectively, resulting in greatly reduced errors.

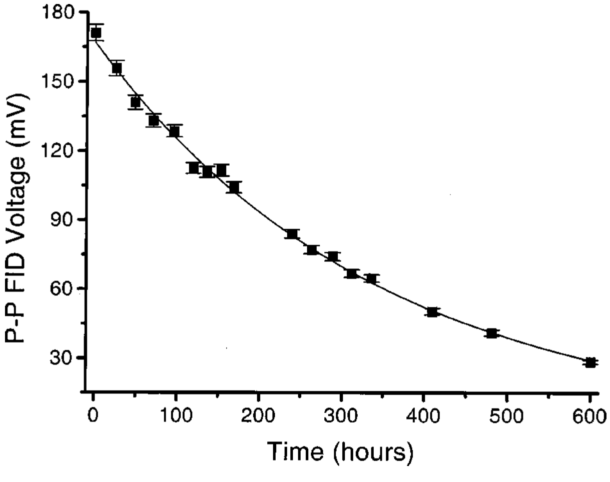

FIG. 2. A signal proportional to polarization is shown as function of time for cell C, the coated Pyrex cell. The spin-down, which corresponds to trial No. 8 of Table I, exhibited the longest T_1 (344±8 h) of any gaseous sample that we have measured.

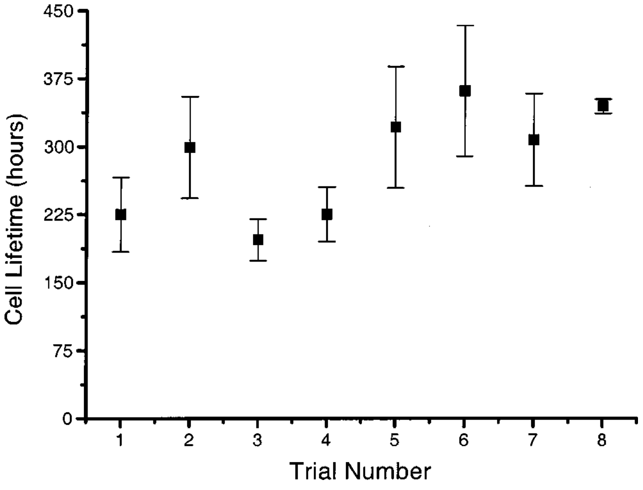

FIG. 3. The measured T_1's are shown as a function of trial number for cell C, the coated Pyrex cell.

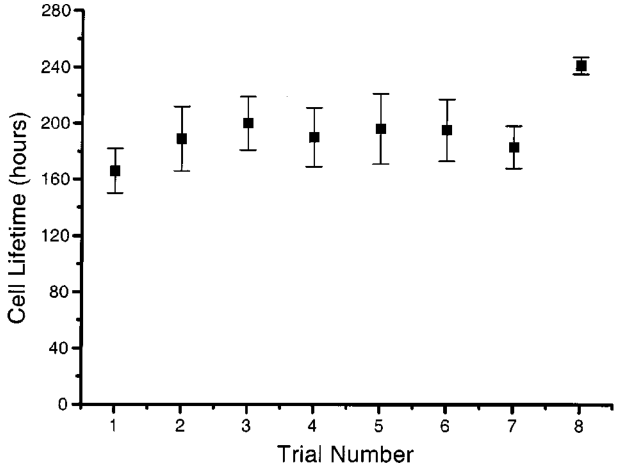

FIG. 4. The measured T_1's are shown as a function of trial number for cell D, the uncoated Pyrex cell.

Our results are summarized in Table I and plotted in Figs. 3 and 4. Cells A and B were made of aluminosilicate glass and coated with a 50% alumina coating. They were filled to approximately 11.2 and 2 atm, respectively. Cell A appeared to have a 50 h T_1 initially, but deteriorated to roughly 23 h. Cell B was always around 20 h.

Cells C and D were both made of Pyrex, and showed markedly longer T_1's than either cells A or B. They were filled to 1.9 and 2.0 atm of ^{3}He, respectively. Cell C was coated with a 20% alumina coating, and cell D was left uncoated as a control. When choosing the composition of the sol-gel coating for the Pyrex cell, we were careful to ensure that the coefficient of thermal expansion would be smaller than that of Pyrex. We reasoned that this would ensure that the coating would be put under compression as the cell cooled following densification in the furnace. We were concerned that putting the coating under tension could result in the formation of cracks. With cells A and B we took no such precautions, and the coefficient of thermal expansion of the coating was slightly larger than that of the cell. Cracking is a reasonable hypothesis for the relatively poor performance of cells A and B.

The T_1's of cell C appear to show an upward trend with trial number, yielding a T_1 of 344 ± 8 h in trial No. 8, remarkably close to the 392 h that Newbury *et al.* would predict for relaxation in the bulk alone. This is the longest T_1 we have ever measured for a gaseous sample, as well as the longest spin-down we have ever conducted. We interpret the good performance over repeated trials as an indication that the reactivity of the Rb with the sol-gel coating did not limit the performance of our sample. The excellent performance of the uncoated Pyrex cell came as a mild surprise. The T_1's reported in the literature for Pyrex in the presence of alkali metals have varied widely from about 3 h[9] to more than 60.[10] Timsit *et al.* showed that Pyrex yielded short T_1's for ^{3}He, an observation that they attributed to the high porosity of Pyrex to ^{3}He.[11] Timsit *et al.* polarized ^{3}He using metastability exchange, however, which does not involve the use of alkali metals, so their results may not be directly relevant to this work. It is also possible that the purity of Pyrex has improved in the nearly 30 years since their work.

In conclusion, we have established a sol-gel coating technique that can yield very long T_1's for ^{3}He that is polarized by spin-exchange optical pumping. Because our substrate was Pyrex, which is easy to work, our results have the potential for making the polarization of ^{3}He by spin-exchange optical pumping more practical. We have also observed that uncoated Pyrex, under certain conditions, yields very good results, an interesting result by itself. Finally, we are hoping that the high purity that can be obtained with sol-gel coatings will make it possible to fabricate cells with greater reproducibility, regardless of the substrate material. We anticipate that sol-gel coatings will be of great practical value both in fundamental research as well as in medical imaging.

The authors would like to acknowledge many useful discussions with W. Happer. This work was supported by the U.S. Air Force Office of Scientific Research, Grant No. F49620-98-0127, the U.S. Department of Energy, Grant No. DE-FG02-90ER40557, and a MRSEC grant funded by the NSF (Grant No. DMR 9809483).

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