APPLICATION OF SOL-GEL TECHNOLOGY TO HIGH PRESSURE POLARIZED ^{3}HE NUCLEAR TARGETS

W. A. TOBIAS, G. D. CATES, J. CHAPUT, A. DEUR, S. ROHRBAUGH
AND J. SINGH

Department of Physics,
University of Virginia,
P.O. Box 400714,
Charlottesville, VA, USA
E-mail: wat4y@virginia.edu

High-purity sol-gel solutions have been developed to coat the interior surface of glass vessels used for polarizing ^{3}He by spin-exchange optical pumping. Such cells have been shown to exhibit ^{3}He longitudinal lifetimes T_1 in excess of 350 hours[1]. The sol-gel technique was designed to minimize spin-relaxation due to wall collisions so that only dipole-dipole interactions between colliding ^{3}He atoms dominate in the relaxation process. Until now, sol-gel technology had not been applied to high pressure ^{3}He gas targets used in nuclear scattering experiments. A description of the sol-gel technique and recent developments on its integration into the production of ^{3}He targets will be presented.

1. The Polarization Process

1.1. *Spin-Exchange Optical Pumping*

In order to polarize high density (10 amg) ^{3}He targets, the *spin-exchange optical pumping* technique is used[2]. It consists of polarizing a low density vapor of rubidium by optical pumping. This electronic polarization is subsequently transferred to ^{3}He nuclei through spin-exchange collisions.

A simplified level diagram for the ground and first excited states of the rubidium atom in the presence of a magnetic field is shown in figure 1. Here, the Rb nuclear spin has been neglected. The valence electrons are excited from the $5S_{\frac{1}{2}}$ ground state to the $5P_{\frac{1}{2}}$ first excited state by way of circularly polarized light. It is tuned to the Rb D1 wavelength of about 794.8nm where its polarization is parallel to the magnetic holding field. The electrons decay back to both ground state levels with equal probabilities. In all, within milliseconds, one of the $m=\pm\frac{1}{2}$ spin substates of the ground state level is depopulated. This results in an electron spin polarization of rubidium, typically greater than 90% for these targets. A small amount (70

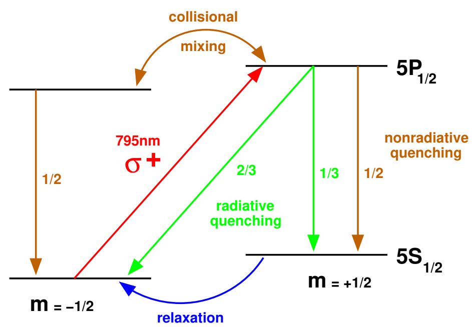

Figure 1. Energy level diagram for rubidium in an external field and assuming I=0.

torr) of N_2 buffer gas is added to help nonradiatively quench the excited electrons and improve the optical pumping process.

Spin exchange between Rb and ^{3}He occurs when the polarized Rb atoms undergo binary collisions with the ^{3}He atoms, transferring angular momentum via a hyperfine interaction.

1.2. ^{3}He *Polarization Measurement*

The target polarization can be monitored using adiabatic fast passage (AFP), a nuclear magnetic resonance (NMR) method[3]. The ^{3}He nuclear spin direction is adiabatically reversed and the signal induced amplitude in a pair of pick-up coils near the target is proportional to the helium nuclear polarization.

1.3. ^{3}He *Polarization Growth*

For a spin exchange rate γ_{SE}, the ^{3}He polarization build-up follows the functional form:

$$P_{\mathrm{He}} = P_{\mathrm{Rb}} \frac{\gamma_{SE}}{\gamma_{SE} + \Gamma_{\mathrm{He}}} \left[1 - e^{-(\gamma_{SE} + \Gamma_{\mathrm{He}})t} \right] \tag{1}$$

Here, P_{Rb} is the average rubidium polarization and Γ_{He} is the ^{3}He relaxation rate. The saturation in polarization is an equilibrium between the spin-exchange rate and the ^{3}He depolarization rate. Minimizing the decay rate Γ_{He} maximizes the ^{3}He polarization. Figure 2 shows a typical polarization build-up (spin-up) of a ^{3}He target cell. Polarizations of about 45% have been attained.

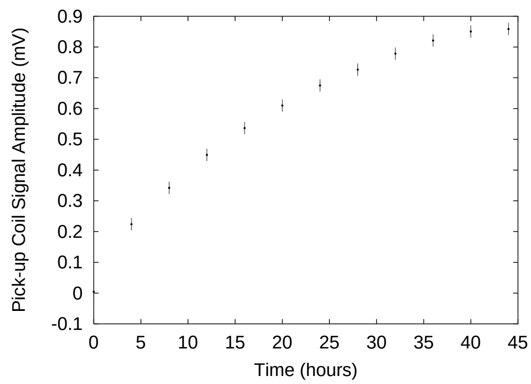

Figure 2. Spin-up of nuclear target cell.

1.4. ^{3}He *Polarization Relaxation Mechanisms*

The helium polarization lifetime in the absence of optical pumping is often defined as the reciprocal of the relaxation rate Γ_{He}. A longer lifetime is an indication of higher cell quality. The polarization decay has the functional form:

$$P_{\mathrm{He}} = P_o e^{-\Gamma_{\mathrm{He}} t} \tag{2}$$

where a decay measurement (spin-down) is shown in figure 3. Typical acceptable lifetimes range from 40-60 hrs, where lifetimes high as 70 hrs have been achieved. Dipolar, wall and field gradient relaxation mechanisms determine the ^{3}He polarization decay rate.

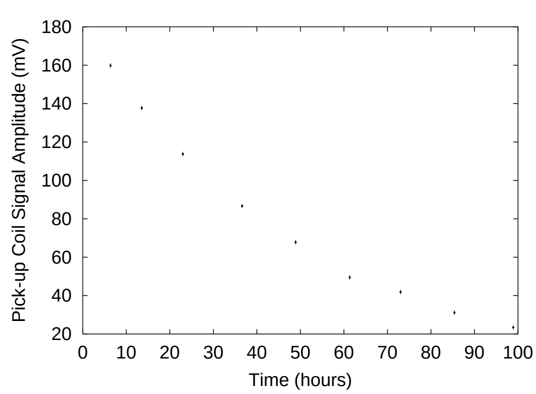

Figure 3. Spin-down of nuclear target cell.

The dipolar and wall relaxation processes act as the dominant relaxation mechanisms. Binary collisions between two ^{3}He atoms result in a magnetic-dipole interaction that couples the nuclear spins to the relative angular momentum of the pair. As a result, nuclear polarization may be lost to orbital angular momentum. This dipolar relaxation rate is[4]:

$$\Gamma_{dipolar} = \frac{[^3\mathrm{He}]}{744}\mathrm{hr}^{-1} \tag{3}$$

where the density of ^{3}He is in amagats, defined as the density of gas at STP. This sets the lower bound to the helium decay rate, hence an upper bound on the lifetime. 74.4 hours is the maximum lifetime attainable for a 10 amg ^{3}He cell. Moreover, imperfections and impurities in the cell walls can have depolarizing effects which contribute to the wall relaxation rate. This rate can vary depending on glass quality and cleanliness. Inhomogeneities in the target holding field contribute an external source of depolarization which is negligible when a large pair of helmoltz holding coils (about 1.5m in diameter) is utilized and all ferromagnetic materials from the vicinity of the target are removed.

Together, the dipolar, wall and field gradient mechanisms make up the total decay rate at room temperature:

$$\Gamma = \Gamma_{dipolar} + \Gamma_{wall} + \Gamma_{field} \tag{4}$$

With a negligible contribution from field gradients and a lower bound set by the dipolar relaxation, wall effects can dominate in the relaxation rate. The goal is to minimize wall relaxation so that only the dipolar mechanism dominates.

2. Target Cell Properties

Glass cells are the vessels used to contain the ingredients for polarizing ^{3}He-gas via spin-exchange optical pumping. The use of glass allows transmission of 794.8nm laser light into the cell. The helium target cells contain gas at high pressure; 8-10 atm ^{3}He, 70 torr N_2 and a few hundred milligrams rubidium. A nuclear cell is shown in figure 4.

The glass should contribute minimally in the way of wall relaxation processes. Therefore, one would like to use glass that contains little or no *paramagnetic impurities*. Also, any cracks or *microfissures* on the glass wall increase the number of interactions and interaction time between ^{3}He nuclear spins and surface atoms which cause depolarization. A smooth paramagnetic-free surface is optimum.

Also, the glass must be reasonably impermeable so that ^{3}He leakage is minimized.

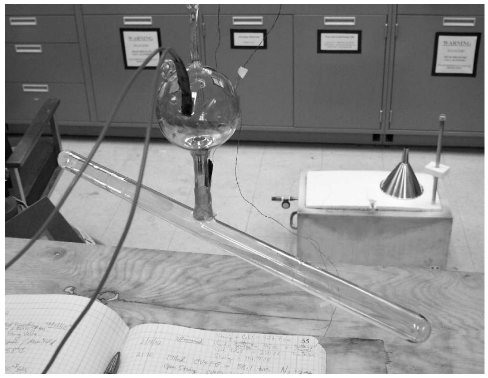

Figure 4. Sol-gel coated nuclear target cell.

3. Sol-Gel

Sol-gel processing is a method by which one can obtain glass via a chemical route at low temperature from a liquid solution. With this procedure, one can acheive better homogeneity and higher purity than are possible with standard glass making processes. In case of film production, one has more precise control over thin glass microstructure. The goal is to coat target cells with a thin layer of pure aluminosilicate glass to decrease the wall relaxation by way of minimizing any paramagnetic impurities, porosity, and microfissures.

3.1. *Chemistry*

In large part, glass consists of an amorphous silica network. One can synthesize such a structure by chemical means using liquid silicon precursors called *silicon alkoxides*[6]. A typical procedure involves filling a glass cell with a solution of tetraethyl orthosilicate (TEOS): $SiO_4(C_2H_5)_4$, water: H_2O, and ethanol: C_2H_5OH. *Hydrolysis* of alkoxide groups (OR where $R=C_2H_5$) occurs when the TEOS readily reacts with the water during mixing of the solution:

$$\equiv \mathrm{Si} - \boxed{\mathrm{OR} \quad + \quad \mathrm{H}} - \mathrm{OH} \quad \Longrightarrow \quad \equiv \mathrm{Si} - \mathrm{OH} \quad + \quad \mathrm{ROH} \tag{5}$$

Condensation produces siloxane bonds (Si-O-Si) with water and alcohol by-products. This leads to the formation of the amorphous silica network, the wet gelation of the sol:

$$\equiv \mathrm{Si} - \boxed{\mathrm{OH} \quad + \quad \mathrm{H}}\mathrm{O} - \mathrm{Si} \equiv \quad \Longrightarrow \quad \equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv \quad + \quad \mathrm{H_2O} \tag{6}$$

$$\equiv \mathrm{Si} - \boxed{\mathrm{OH} \quad + \quad \mathrm{R}}\mathrm{O} - \mathrm{Si} \equiv \quad \Longrightarrow \quad \equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv \quad + \quad \mathrm{ROH} \tag{7}$$

Drying of the gel leads to the formation of a xerogel, shrunken dry gel layer. Heating the xerogel to a high temperature, typically about 550^{o}C, *sinters* the gel to form a densified glass film layer $\sim$200μm (figure 5).

Since we wish to produce an *aluminosilicate* or Al_2O_3-SiO_2 network, the solution with which we fill the cells is doped with aluminum nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$. The concentration of $Al(NO_3)_3 \cdot 9H_2O$ in the solution was choosen so that the sol-gel film layer has a slightly smaller coefficient of thermal expansion than the glass substrate so that the glass film remains under compression through repeated heat cycles. For Pyrex and GE-180, we used 20% and 25% alumina (mole % Al_2O_3) composition, respectively.

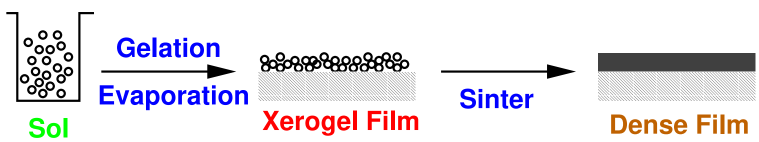

Figure 5. The sol-gel process.

4. Experiment

Studies were performed at the University of Virginia that complimented the study done by Hsu *et al*[1]. The studies included fabricating coated and uncoated GE-180 1-inch diameter spherical cells and a coated Pyrex nuclear target cell and testing their quality by measuring the lifetime. Sol-gel coating aluminosilicate small cells and a large nuclear target cell have been attempted before without success. The Virginia study is the first to succeed.

The appropriate sol-gel chemical ingredients were mixed in an ehrlemeyer flask and continuously stirred for several days. The cells were then filled with the solution and allowed to sit for about three hours. The cells were then emptied and allowed to air dry for another three hours, put in an oven at 60^{o}C overnight and then the next day sintered at 550^{o}C for two hours. Each cell was coated twice using this method. Then, the cells were attached to a gas system and pumped on and baked at about 420^{o}C for just under a week. On the day the cell was filled, Rb was first distilled into the cell and then N_2 and ^{3}He gases were condensed into the cell by submerging them into a LN_2 or LHe bath.

Several 1-inch diameter spherical GE-180 glass cells were either coated with sol-gel or left uncoated and filled to about 2.5 amg of ^{3}He, and a nuclear target sized sol-gel coated Pyrex cell (*Charlie*) was filled to about 8.4 amg.

5. Results

Table 1 presents the lifetime measurements from the University of Virginia experiments on aluminosilicate and are compared to the Princeton[1] results on Pyrex. They indicate good lifetime results for all the sol-gel coated cells and show that the wall relaxation is significantly reduced and is comparable to the Princeton results. The last column contains results on the target cell.

Table 1. Lifetime results for small spherical cells and the sol-gel coated nuclear target cell.

	Glass (Cell)	Density	Lifetime	$\Gamma_{dipolar}$	Γ_{wall}
Princeton:	coated Pyrex (C)	1.9 amg	344±8 hrs	1/392 hrs^{-1}	1/2809 hrs^{-1}
	uncoated Pyrex (D)	2.0 amg	241±6 hrs	1/372 hrs^{-1}	1/684 hrs^{-1}
	coated GE-180 (8)	2.4±0.1 amg	278±10 hrs	1/310 hrs^{-1}	1/2693 hrs^{-1}
Virginia:	coated GE-180 (5)	2.5±0.1 amg	262±10 hrs	1/298 hrs^{-1}	1/2169 hrs^{-1}
	uncoated GE-180 (9)	2.5±0.1 amg	116±6 hrs	1/298 hrs^{-1}	1/190 hrs^{-1}
nuclear cell	coated Pyrex (T)	8.4±0.2 amg	53±2 hrs	1/87 hrs^{-1}	1/136 hrs^{-1}

6. Conclusion

The sol-gel coatings seem to improve average lifetime performance in small cells. We have also demonstrated successful application of sol-gel technology to full sized target cells. We hope sol-gel films will provide a *standardized* high purity surface while other optically pumped spin-exchange target system problems are pursued.

References

1. M. F. Hsu *et al*, *Appl. Phys. Lett.* **77**, 2069 (2000).
2. W. Happer *et al*, *Rev. Mod. Phys.* **44**, 169 (1972).
3. A. Abragam, *Principles of Nuclear Magnetism*, Oxford University Press, (1961).
4. N. R. Newbury *et al*, *Phys. Rev. A* **48** 4411, (1993).
5. G. D. Cates, *Phys. Rev. A* **37** 2877, (1988).
6. C. J. Brinker and G. W. Scherer, *Sol-Gel Science*, Academic Press, (1990).