Long Longitudinal Relaxation Time Silicon Nanoparticles

Shawn Wagner[1,2], Denis Avdic[1], Alexander Grunfeld[3], and Debiao Li[1,2]

[1]*Biomedical Sciences, Cedars-Sinai Medical Center, Los Angeles, California, United States,* [2]*Biomedical Imaging Research Institute, Cedars-Sinai Medical Center, Los Angeles, California, United States,* [3]*Life Sciences, UCLA, Los Angeles, California, United States*

TARGET AUDIENCE: Scientists interested in imaging and molecular targeting of magnetic resonance materials who would like to have an overview of the scientific and technical foundation of solid state hyperpolarization.

PURPOSE: Knowledge of the longitudinal relaxation time (T_1) of nanoparticles is useful for developing long lived nuclear magnetic resonance (NMR) signal for molecular targeting. Currently, dynamic nuclear polarization (DNP) has been employed to increase the NMR signal by 30,000-100,000 times the normal signal. This has been useful for obtaining metabolic data for the utilization of ^{13}C-pyruvate in cell cultures and *in vivo* animal models.[1,2] However, the T_1 of pyruvate is about 35 seconds which limits this molecule from being an effective tracking agent or molecular marker. Other ½ spin nuclei like yttrium (^{89}Y) and silicon (^{29}Si) can have much longer T_1 values. Recent literature has suggested that the T_1 value in silicon particles is size dependent because the dominate relaxation is a result of spin diffusion from the surface to the core.[3,4] The hypothesis was that oxygen serves as a relaxation source for the surface silicon nuclei and dipole–dipole coupling between 29-silicon drives relaxation into the core of the particles by spin diffusion. In this work, we measured the T_1 values of silicon nanoparticles of various sizes to verify whether the hypothesis is true.

METHODS Four polycrystalline silicon powders were acquired from US Research Nanomaterials, Inc. These particles represent different size ranges, different surface areas, different impurities and different manufacturing processes. The one thing they all have in common is that the surfaces of these particles oxidize to form an oxide layer. The silicon powders were packed in 5mm diameter borosilicate NMR tubes cut to a length of 4 cm. A saddle coil tuned to the ^{29}Si resonance (79.5 MHz) was used for acquisition in a 9.4T Bruker BioSpec magnet. The magnetic field was shimmed with a water sample placed in the coil using a large ^{1}H transmit/receive coil. The same shim settings were used for all silicon samples. A saturation recovery experiment was used to acquire the T_1 relaxation saturation recovery curves. Briefly, the sample was saturated with sixteen 90 degree pulses, a variable delay was applied and a 90 degree read pulse was used to acquire one time point. 12 data points ranging from 6.33 to 180 minutes were used to calculate the T_1 relaxation, time points below 6.33 minutes were not used in order to remove contributions of the silicon peak from the borosilicate glass (small T_1 value). The six longest recovery acquisitions were used to measure the line widths of the spectra for each particle size.

RESULTS We recorded an increase in T_1 relaxation with decreasing particle size (T_1±std. err. (minutes): 1-3 µm; 21.7±6.0, 100 nm; 41.9±12.0, 50-70 nm; 84.5±27.2, 30-50 nm; 87.1±18.7). The line width of the ^{29}Si resonance peak decreased with decreasing particle size (l.w. ± std. dev. (Hz): 1-3 µm; 1196±92, 100 nm; 383±55, 50-70 nm; 218±21, 30-50 nm; 225±17).

DISCUSSION Our data does not corroborate prior published data which demostated that the relaxation of ^{29}Si in nanoparticle is strongly correlated to size and that relaxation time should decrease with decreasing particle size. According to the calculation presented[4], the relaxation rate of the 30-50 nm particles would be 1.4 to 4.0 minutes which is not consistent with the >80 minutes that we have measured. The decreasing line width with the decreased size is an indication that smaller nanoparticle have a greater crystalline composition which would result in longer relaxation times.

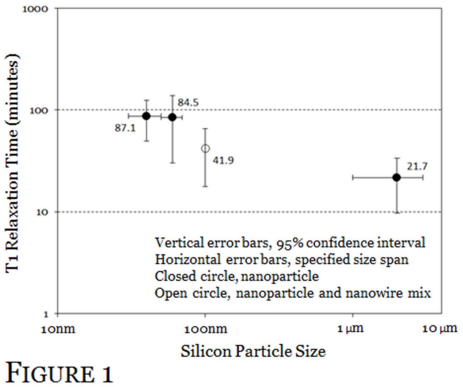

FIGURE 1

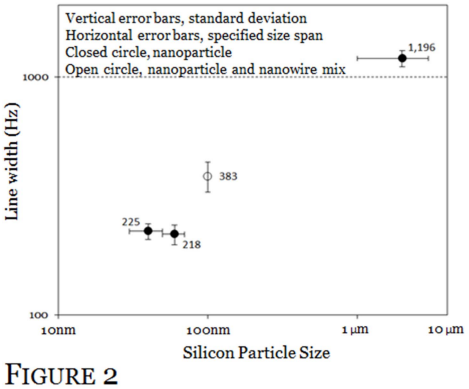

FIGURE 2

CONCLUSION Small nanoparticles have longer than predicted relaxation times and would be suitable for development into molecular targeting agents which could be followed for several hours.

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