

Method development for producing thin ^{14}C foils

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Abstract. Thin, isotopic ^{14}C foils are of great interest to the nuclear physics community as neutron-rich targets. Historically, these foils have been extremely difficult to prepare and an effort is underway to make them readily available. The stock material of ^{14}C available at Argonne contains a number of oxide impurities (SiO_2 , MgO , and Al_2O_3), which affect the composition and stability of the fabricated foil. A simple, robust method was developed (using ^{13}C as a surrogate) to purify the ^{14}C material while minimizing loss and potential spread of the material. Thin foils were fabricated using the purified carbon, the unpurified carbon/oxide mix, and purchased high-purity carbon powder. SEM and EDS of the resulting foils was performed and the efficacy of this purification method was demonstrated.

1 Introduction

There is heavy interest in having low- Z , neutron-rich targets such as ^{14}C , particularly for studying nuclear structure of neutron-rich radionuclides and for astrophysical research experiments. Argonne National Laboratory has a stock of ^{14}C material identified for making nuclear physics targets. This material is legacy material from Los Alamos National Laboratory's pion program and was reported as containing 75% ^{14}C , 16% ^{12}C , and 9% impurities (magnesium oxide, aluminum oxide, and silicon oxide). Preliminary targets made utilizing a mixture of natural carbon with these impurities were found to have some issues with stability and degradation during production. To provide beam-stable, thin ^{14}C target, a purification method was devised to remove the bulk of these impurities prior to preparing the foil. This publication presents some interesting early results in this process.

2 Methods and materials

2.1 Materials

Carbon powder, magnesium oxide, aluminum oxide, and silicon oxide powders were all purchased from Sigma-Aldrich (St. Louis, Missouri). Aluminum foil was purchased from Goodfellow (Coraopolis, Pennsylvania). Sodium hydroxide (50% w/w) and isopropanol were purchased from Sigma-Aldrich and used as provided without further purification. A special binder mixture was prepared for making the carbon foils; a 5% w/w dispersion of ethyl cellulose in 80:20 toluene: ethanol (cP 300; Sigma Aldrich) was further diluted with isopropanol to the desired 2.5% w/w concentration. All

water was purified on-site using a Millipore system set to greater than $18\text{ M}\Omega\cdot\text{cm}$.

2.2 Removal of impurities

With the ^{14}C stock material containing oxide impurities, a simple, glove-box-friendly method was developed to remove the bulk of these impurities. A homogenized test mixture of bulk, natural carbon with magnesium oxide, aluminum oxide, and silicon oxide added as impurities was prepared and an aliquot was transferred to a 50 mL centrifuge tube. NaOH (50% w/w) was added and gently stirred to incorporate. The tube was shaken several times over the course of a day to ensure interaction of the material with the NaOH and set aside to settle overnight. Gravitational settling was selected over centrifugation due to space limitations for equipment in the glovebox. As the material settled, a white oxide layer settled on top of the bulk carbon; this oxide layer was pipetted away for one sample and left intact for an additional sample. Once the material had settled, the liquid was pipetted off and fresh deionized water was added to rinse away the NaOH and dissolved impurities. This was repeated for a total of three water washes. The material was then pipetted into the pre-weighed polypropylene jars using a small amount of isopropanol for the transfer. This material was allowed to completely dry and the mass of the material was then determined prior to preparation of foils.

2.3 Printing the carbon on an aluminum foil

The foils were printed following a graphene printing method that was recently described in the literature [1]. In short, the dried carbon samples were combined with binder and isopropanol to produce the "carbon paint" for preparing targets. All samples were 1: 1: 0.5 by weight

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of carbon: binder: isopropanol. The natural carbon sample used 0.5 g carbon, the purified carbon with oxide removed (PWR) sample used 0.49 g carbon, purified carbon without oxide removed (PWOR) sample used 0.62 g carbon, and the impure carbon sample used a 0.50 g of bulk carbon mixed with the various oxide impurities. Each sample was mixed 3 x 15 seconds in a SpeedMixer at 3000 rpm with 5 minutes of cool down between each run.

Once the paints were prepared, an aluminum foil was set in place on the draw-down machine (Figure 1). 0.5-0.6 mL of the carbon paint was drawn up in a syringe and pipetted across the aluminum foil in front of the Mayer rod. The printer bar was pulled across the surface of the foil to spread a uniform layer of the paint across the surface of the foil. The foils were allowed to air dry for 10 – 15 minutes prior to handling them. Then, each foil was then cut to fit inside of 100 mm diameter petri dishes. The lids were placed, so the remaining organic solvents could escape and the foils were all placed in a 100° C oven for two hours.

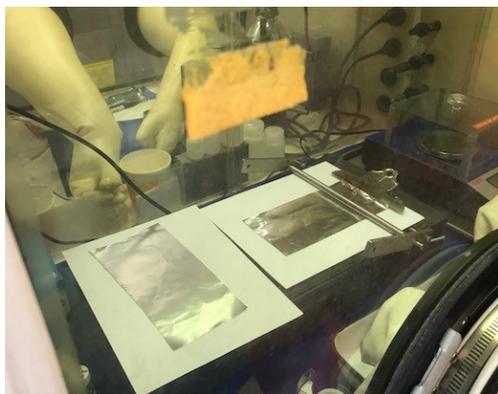


Fig 1. Draw-down machine with Mayer rod set in place on aluminum foil backing.

2.4 Etching away the aluminum and floating targets onto frames

After the foil was baked to set the binder and allowed to cool, pieces of each foil were cut into small 1.5-2 cm squares. The aluminum backing was etched away using a bath containing NaOH (50% w/w). For each foil, this process was 30-40 minutes long. The foil was transferred from the NaOH to a water bath using a microscope slide. The water bath helped to remove remaining NaOH off the target and the targets were floated onto target frames.

2.5 SEM and EDS analysis of the produced foils

Samples were examined by scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDS) analysis to examine the structure of the printed carbon foils and the elemental composition of the pure, purified, and impure samples. SEM and EDS were performed using a Hitachi S-3000N SEM equipped with a Thermo-Noran UltraDry detector and System Seven analysis system and software. Images were taken at 10 keV using a secondary electron detector.

Composition analyses by EDS used a “Proza” ($\phi(\rho z)$) standardless analytical correction, assuming metals (i.e. oxygen was analyzed directly rather than assuming oxides).

3 Results and conclusions

3.1 Removal of impurities

A mock ^{14}C stock feed sample was prepared using natural carbon, magnesium oxide, aluminum oxide, and silicon oxide. A simple dissolution method was developed to remove the impurities and minimize the loss of the valuable, enriched ^{14}C material. The oxides present an interesting chemical processing issue as the magnesium oxide is a basic oxide, aluminum oxide is an amphoteric oxide, and silicon oxide is a weakly acidic oxide, so multiple solvents would be necessary to full dissolve away all the impurities. Since NaOH is part of the process already, it was decided to first begin this process using base to dissolve the silicon oxide and potential a small portion of the aluminum oxide (given a sufficient contact time). After the sample was contacted with the NaOH, it was noted that a white oxide layer formed on the surface of the bulk carbon layer. Assumedly, the larger grain size of the carbon enabled it to sink faster than the finer oxides. In one of the samples, this oxide layer was removed to see how this affected the overall retained impurities (Figure 2). During the NaOH dissolution and the first water wash, an oily carbon layer was observed. This layer shrank with each wash and likely resulted from some the interaction of the base and oxides. The water was significantly clearer after the second water wash (Figure 3). These materials transferred using isopropanol to clean polypropylene jars, allowed to dry, and then used to produce carbon paint for preparing foils. Final determination of purity was performed by SEM and EDS, which is reported later in this paper.

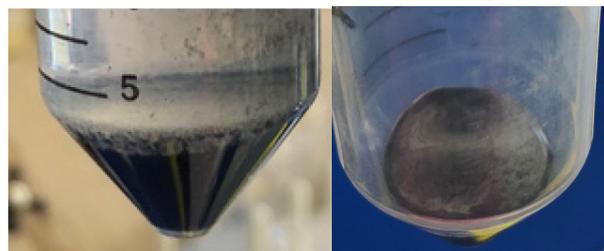


Fig. 2. White oxide layer formed on top of the sample (left) and resulting amount of oxide layer after removal (right). Some losses of carbon due to pipetting.

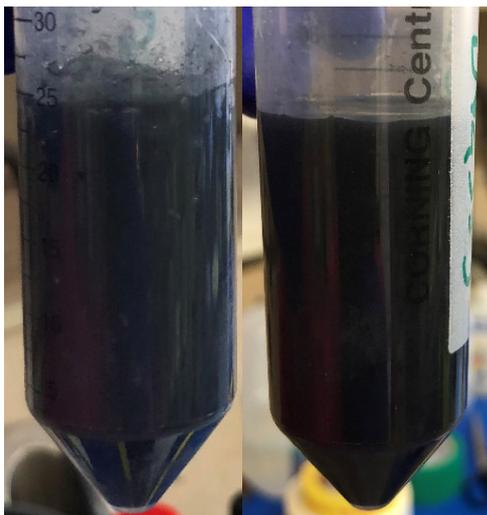


Fig. 3. After the material was combined with NaOH and shaken, note the frothiness and bubbling (Left). After the material was washed a second time with water, the solution is homogenous (right).

3.2 Printing the carbon on an aluminum foil

The carbon powders (natural carbon, purified with oxide layer removed (PWR), purified without oxide layer removed (PWOR), and carbon/impurities mixture) were successfully converted into paint, and foils were prepared for each sample. After the foils were baked, there is a distinct color variance between the various samples (Figure 4). The foils of natural carbon and the PWR sample are similar in color. The PWOR sample is slightly grayer. The unpurified carbon sample is very noticeably grayer than the rest. This suggests the method effectively removed a significant amount of the impurities. Additionally, the brittleness of the target increased with the amount of impurities present (as is evident from the flakiness of the impure foil in Figure 4).

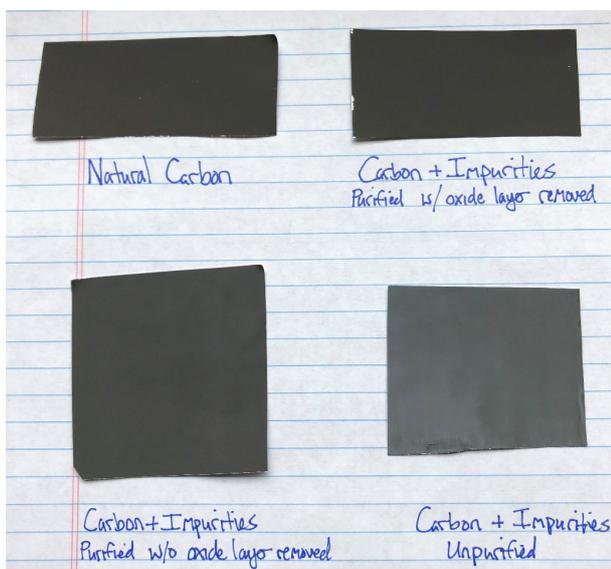


Fig. 4. Foils produced from each carbon sample.

Based on the known areal density of the aluminum foil, the areal density of each foil was determined. Each of the foils were between 2.1-3.2 $\text{mg}\cdot\text{cm}^{-2}$ thick. All foils survived being etched. A vial was placed inside the etching container to keep the foil upright, so the bubbles did not get trapped under the foil surface and damage the foil. Finally, the foils were floated in water and attached to the target frames.

3.3 SEM and EDS analysis of the produced foils

SEM and EDS were performed on sample foils of the various carbon purities. Purely observing the foils under SEM, the PWR sample appears quite similar to the natural carbon sample, the layer is quite defined and the material looks well packed. Conversely, the impure carbon and the PWOR sample show a pitted less structured formation (Figure 5), which explains the brittleness observed when handling the foils.

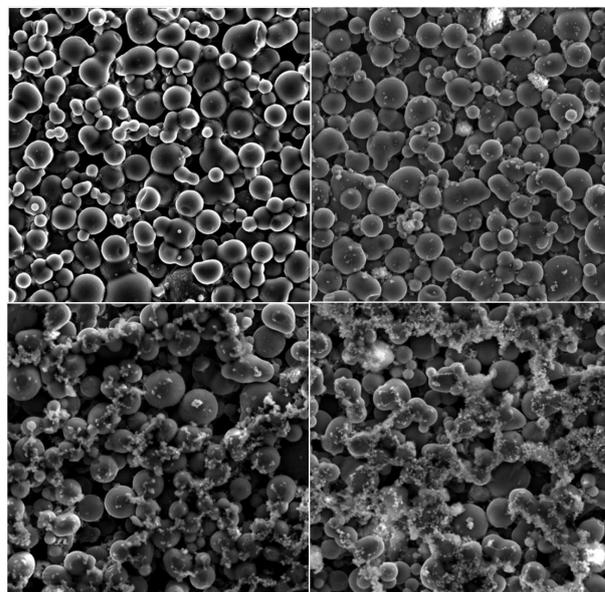


Fig. 5. Comparison of the SEM spectra for all produced foils. Magnification was x1000. Natural Carbon (Top Left), Purified with Oxides Removed (Top Right), Purified without Oxides Removed (Bottom Left), and Impure Carbon (Bottom Right).

EDS was performed on each sample to determine the efficacy of the dissolution method to remove the unwanted impurities. Relative to the impure sample, 99.9% of the silicon dioxide was removed for both methods of oxide removal. This is expected with silicon dioxide being an acidic oxide, it is highly soluble in basic solutions. For the PWOR sample, only a small percentage of magnesium oxide (4.1%) and aluminum oxide (6.5%) were removed. For the PWR sample, 53.9% of the magnesium oxide and 57.3% of the aluminum oxide were removed. Simply pipetting was capable of removing the majority of these impurities, which really lead to a significantly more stable target being produced. Figure 6 shows representative EDS spectra comparing the impure carbon sample versus the PWR sample.

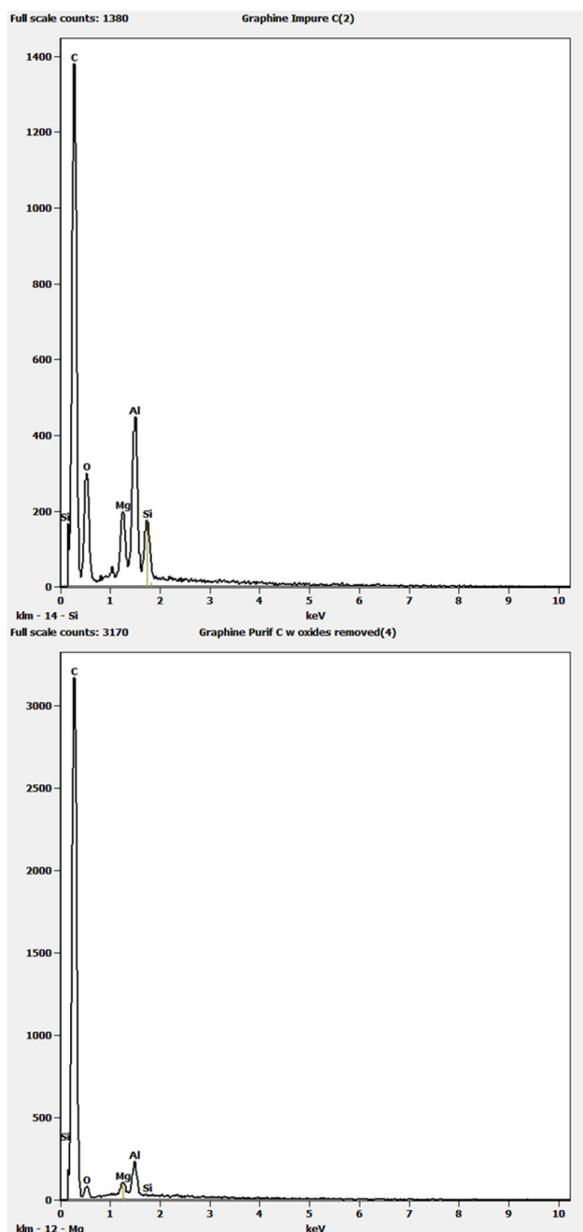


Fig. 6. Comparison of the EDS spectra for the impure carbon (top) and purified carbon with the oxide layer removed (bottom).

4 Conclusions

A simple, glove-box-friendly method was developed to remove the bulk oxide impurities found in the ^{14}C stock material at Argonne National Laboratory. The purified material was utilized in a simple dry down method to produce thin foils for nuclear physics experiments. The produced foils were evaluated by SEM/EDS analysis to examine the structural integrity of the foils and evaluate the reduction of the incorporated oxides. The method successfully produced stable foils with the bulk oxide impurities removed. In the future, additional steps can be added if necessary to improve the dissolution and removal of the magnesium and aluminum oxides.

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References

1. I. Pavlovsky, R.L. Fink, M.D. Gott, and J.P. Greene, AIP Conference Proceedings, **2160**, 040009 (2019)