SCREENING IMPREGNATED CARBON RESPIRATOR MATERIALS *via* THE COMBINATORIAL MATERIALS SCIENCE APPROACH

Jennifer V. Romero, Jock W. H. Smith, Chris L.White and Jeff R. Dahn

Dept. of Physics, Dalhousie Univ., Halifax, N.S. Canada B3H 3J5

Introduction

Activated carbon has long been used as a gas adsorbent for respirator applications. Untreated activated carbon poorly adsorbs low molecular weight, highly polar gases such as HCN, SO_2 and NH_3. The addition of impregnants such us metal oxides, metal chlorides and metal carbonates have been known to react with specific challenge gases within the activated carbon pores facilitating the removal of the toxic gases [1-5]. The addition of a combination of several different impregnants allows a single IAC to adsorb many different toxins well [6-8].

Our goal is to find an optimum set of impregnants to apply to an activated carbon so that a specific set of toxins can be effectively adsorbed. However, finding the right combination of impregnants to prepare optimum IAC's can be time consuming. A strategy for preparing and screening numerous materials simultaneously has been introduced by Joseph Hanak in the 70's [9]. The technique has been adapted to the sputter-deposition of composition-spread thin films for battery, fuel cell and biomaterials applications [10-12]. A combinatorial materials science approach (combi method) for the discovery of an impregnated activated carbon that can adsorb a wide variety of toxic gases (i.e. a multi-gas carbon) has been developed. This approach presently allows the parallel preparation and investigation of 64 to 100 IAC samples at once increasing the rate of discovery of viable multi-gas carbons.

Experimental

A commercially available coconut-shell based granular activated carbon was obtained from Kuraray Chemical Co. The carbon contains 0.4 % (w/w) ash, is slightly basic with a pH of 8 (measured after immersion in nanopure water) and has a mesh size of 12 × 35, which corresponds to particles between 0.50 to 1.70 mm in diameter.

A conventional solutions handling robot (combi robot) was used for this study. Arrays of 64 or 100 samples are prepared by dispensing varying amounts of 2 (or more) solution components on 10 mg samples of activated carbon held in microvials. Impregnation of the carbon samples was accomplished using a method described previously in literature known as the "incipient wetness" or "imbibing" method [5]. A series of heating steps are employed to decompose the impregnants to the desired active phases.

An 8 x 8 array of IAC's was prepared using the combinatorial method described. increasing volumes (from 0 to 3.5 μL) of 3.5 M $Zn(NO_3)_2$•6 H_2O (Sigma-Aldrich) were added in increments of 0.5 μL along x-axis of the 8 x 8 array and increasing volumes (from 0 to 3.5 μL) of 3.5 M $Cu(NO_3)_2$•2.5 H_2O were dispensed in increments of 0.5 μL along the y-axis of the array. A constant volume of 1.0 μL of $H_3PO_4(MoO_3)_{12}$•25 H_2O (0.1 M) was added to all 64 samples. Adequate volume of water was added to each vial to bring the total volume of added liquid to the imbibing limit (8 μL for 10 mg carbon). The vials were capped and then shaken for 5 minutes to ensure complete imbibing and then dried for 2 h under argon at 200 ^oC and 4 h at 120 ^oC in air.

Once the IAC's were completely dried and the final dry mass had been measured, the samples were then exposed to SO_2 gas for 4 h at room temperature. The effectiveness of the samples for adsorbing various toxins is screened gravimetrically by weighing the microvials containing the IAC before and after exposure to the toxic challenge gas. In Figure 1, a detailed flowchart of the combi method is presented. The stoichiometric ratio of reaction (SRR) is calculated from the recorded sample mass increase after exposure.

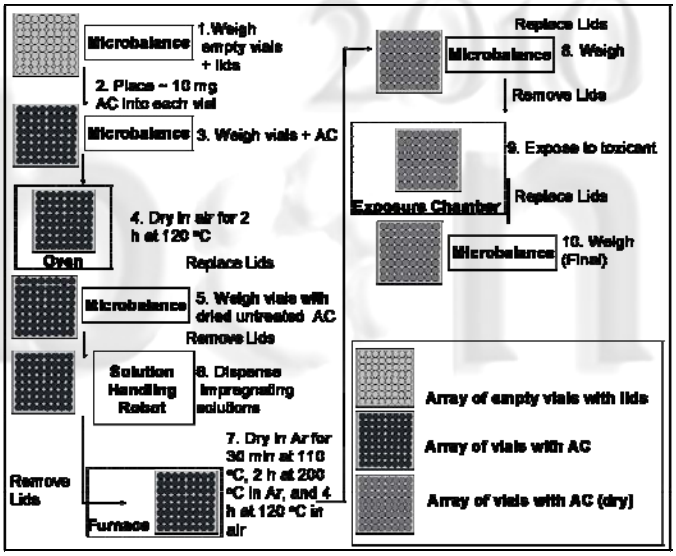

Fig. 1 A detailed process flowchart showing the sample preparation method employed in this study.

Results and Discussion

The method was validated using known gas adsorbent materials such as $ZnCl_2$, K_2CO_3 and CuO-impregnated carbons. The calculated adsorption capacities and stoichiometric ratios of reactions for these known gas adsorbent materials, when evaluated using the combinatorial approach, was comparable to the values obtained using traditional methods of analysis. For $ZnCl_2$, the average stoichiometric ratio of reaction (SRR), defined to be the number of moles of NH_3 captured per mole of $ZnCl_2$ was 1.68 ± 0.09. This value is close to the reported value of 1.6 ± 0.1 obtained from flow tests reported in literature [13]. The SRR's recorded for K_2CO_3 and CuO-impregnated carbons were 1.30

± 0.12 and 0.54 ±0.01 respectively. A library of samples prepared by combining various amounts of CuO and ZnO impregnants showed the expected decreasing trend in the calculated stoichiometric ratio of reaction with respect to increasing amount of impregnants added. In figure 2, trends in the stoichiometric ratio of reaction and gas adsorption capacity relative to the added impregnants is presented for this novel system. The method is now ready to use to explore new systems of impregnated activated carbons.

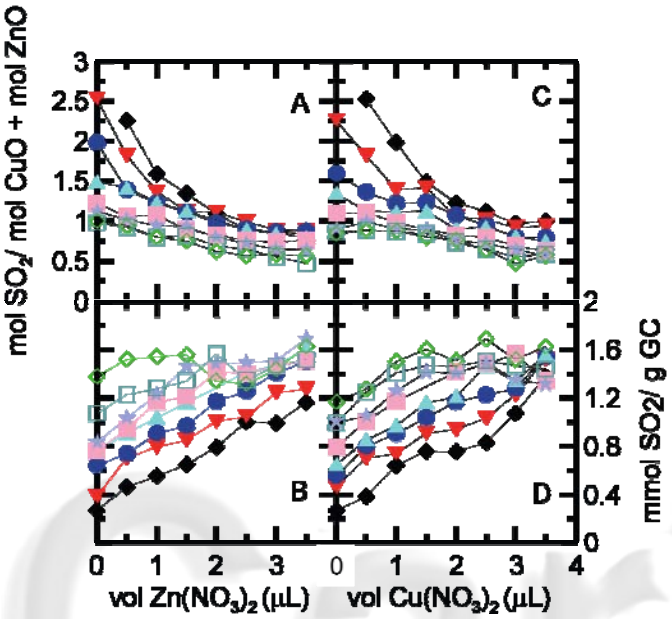

Fig. 2 Plots of A.) SRR (mol SO_2/ mol CuO + mol ZnO) with respect to $Zn(NO_3)_2$; B.) SO_2 adsorption capacity (mmol SO_2/ g GC) with respect to $Zn(NO_3)_2$, C.) SRR (mol SO_2/ mol CuO + mol ZnO) with respect to $Cu(NO_3)_2$ and D.) SO_2 adsorption capacity (mmol SO_2/ g GC) with respect to $Cu(NO_3)_2$. Individual curves in the graphs are plotted according to the specific volume of the second component added. Legend: ♦ 0.0 µL, ▼0.5 µL, ●1.0 µL, ▲1.5 µL, ■2.0 µL, ★2.5 µL, □3.0 µL, ◇3.5 µL of either $Cu(NO_3)_2$ (in graphs A and B) or $Zn(NO_3)_2$ (in graphs C and D).

Conclusions

Known gas adsorbent materials such as $ZnCl_2$, K_2CO_3 and CuO-impregnated carbon materials were successfully prepared *via* the combinatorial approach. These materials were analyzed by the gravimetric method resulting in a faster rate for screening of potential multi-gas adsorbents. The calculated adsorption capacities and stoichiometric ratios of reaction for these materials were comparable to the values obtained from bulk prepared samples using traditional methods of analysis. The preliminary result obtained from the library of samples prepared by combining various amounts of CuO and ZnO impregnants indicated that this method of sample preparation and analysis can effectively screen for viable multi-gas adsorbent materials.

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