Study of space charge regions in $BaCe_{0.8}Y_{0.2}O_{3-\delta}$ - $Ce_{0.8}Y_{0.2}O_{2-\delta}$ hydrogen separation membrane via atom probe tomography

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Ceramic hydrogen separation membranes could offer a low cost, energy efficient alternative to current energy intensive hydrogen separation techniques. The 50/50 wt.% dense composite ceramic, $BaCe_{0.8}Y_{0.2}O_{3-\delta}$ - $Ce_{0.8}Y_{0.2}O_{2-\delta}$ (BCY-YDC), can be synthesized via solid state reactive sintering and has functioned at high hydrogen fluxes [1]. Under a reducing atmosphere, YDC acts as an electron conductor and BCY as an ion conductor. Hydrogen molecules dissociate into H+ ions and electrons and the charges travel through their respective phases and recombine on the opposite side of the membrane to form pure hydrogen gas. Like a number of other technologically relevant conducting oxides, electron and ion conductivity in BCY-YDC is impeded by the formation of space charge regions at grain boundaries (GBs) [2]. Characterizing grain and phase boundaries in BCY-YDC is essential in further improving the GB conductivity and therefore the overall hydrogen flux.

Due to challenges related to directly quantifying chemical composition, particularly oxygen, across general three-dimensional boundaries, atom probe tomography (APT) is one of the only techniques available. The technique is particularly useful in identifying compositional changes across GBs, and has even been used recently to quantify the 3-D space charge voltages around GBs of an ionic conducting oxide [3]. The compositional nature of both GBs and phase boundaries in BCY-YDC are explored in this work using APT. In all cases, deviations in concentrations of cations, oxygen, and impurities around the boundary regions are studied with the goal of relating structure and composition to macro-scale performance. Correlative transmission electron microscopy (TEM) was used to provide complementary information and assist in APT reconstruction accuracy. An example of a BCY GB is found in Figure 1. TEM images were taken before and after APT analysis and overlaid in Figure 1(a). APT analysis of the same tip was performed (Figure 1(b)) and segregation of oxygen vacancies, Ba, Y and Al impurities as well as a depletion of Ce cations are discovered when looking at a region of interest around the GB.

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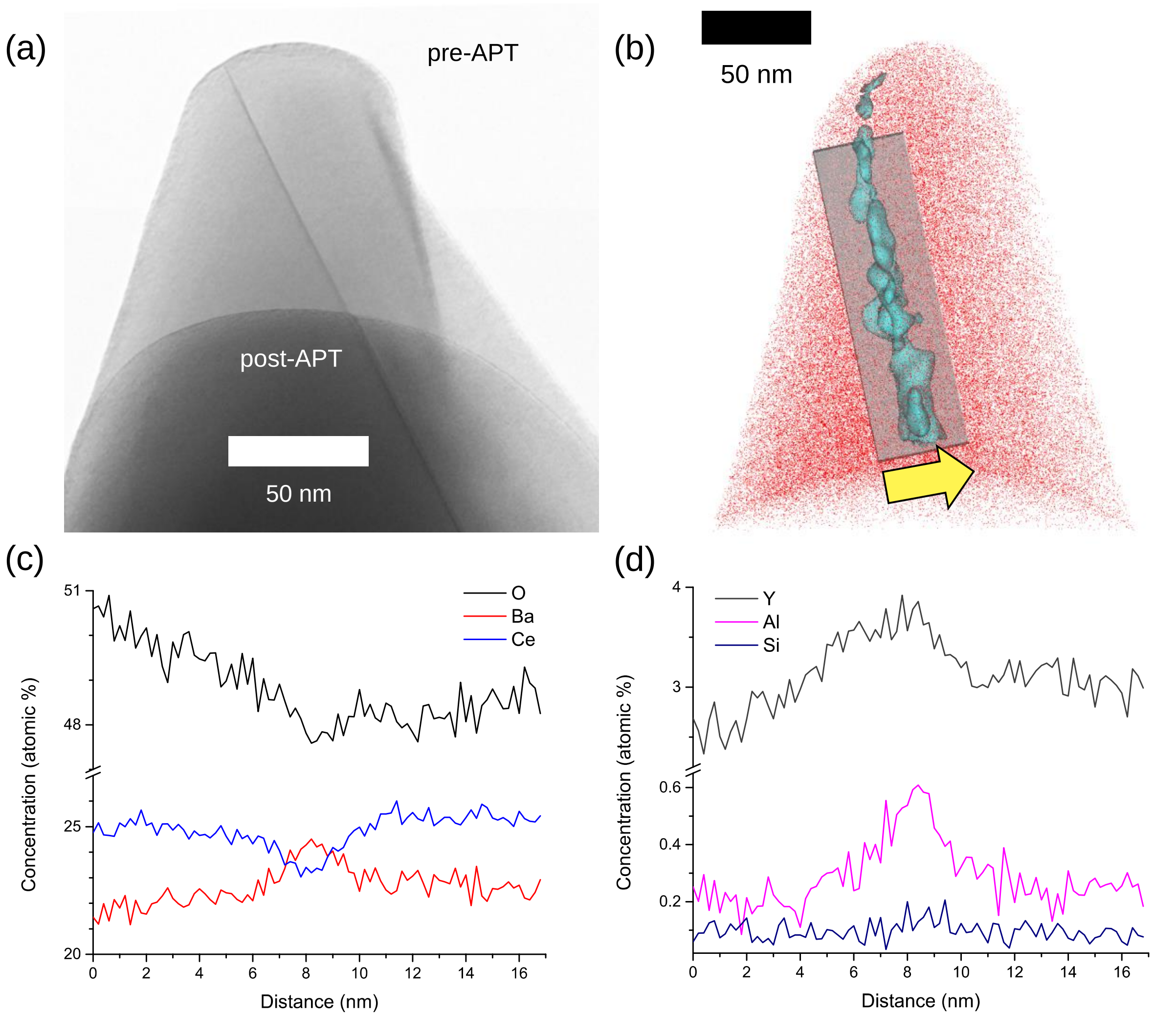

Figure 1. (a) Bright-field TEM image overlay of a BCY GB at the apex of the specimen before (light) and after (dark) APT analysis (b) 3-D APT reconstruction of the same GB as (a). A fraction of the Ce ions in red, 0.19 at% Al isoconcentration surface in blue highlighting the GB. (c) Compositional analysis of O, Ba and Ce through the region of interest (grey box shown in (b)) across the grain boundary. (d) Compositional analysis of Y, Al and Si through the region of interest (grey box shown in (b)) across the grain boundary.