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Title: Alkali Metal Diffusion Through Porous Metal Electrodes in AMTEC Cells

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The mechanisms of mass transport of an alkali metal through porous metal electrodes in alkali metal thermal-to-electric converter (AMTEC) cells is important in optimizing these high current density devices, but also affords the opportunity to investigate a variety of simple mass transport modes at high temperatures via electrochemical techniques. We have previously reported evidence of ionic, free molecular flow, and surface transport of sodium in several types of AMTEC electrodes. Quantitative investigations of Na transport through $WPt_{3,5}$ via surface or grain boundary diffusion, and K transport through porous Mo electrodes by free molecular flow, over large ranges of temperature have been performed. $WPt_{3,5}$ has especially low transport impedance over the 950 to 1200K temperature range. New results are the Na through porous $WPt_{3,5}$ and K through porous Mo diffusion rates and mechanisms.

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The mechanisms of mass transport of an alkali metal through porous metal electrodes in the alkali metal thermal-to-electric converter (AMTEC) is an important issue because mass transport losses can result in an unacceptably high internal impedance and lowered output power in this high current density device. The fundamental study of a variety of alkali metal mass transport modes at high temperatures through porous electrodes is also of interest. These processes are fairly conveniently studied by electrochemical techniques because both mass transport and interracial kinetics are comparatively fast. We have previously reported evidence of sodium transport via ionic conduction in Mo/ Na_2MoO_4 and W/ Na_2WO_4 electrodes; by free molecular flow in thin, oxide-free Mo and W electrodes; and evidence for thermally activated surface transport of sodium in Mo electrodes at higher frequencies and in WRh_2 electrodes under d.c. conditions. [1-4]

We have recently reported the high temperature conductivity of potassium β -alumina solid electrolyte (K-BASE) ceramic to be close to that, of its sodium analog at $T > 700\text{K}$. [5] The ceramic was prepared by the KCl vapor ion exchange reaction of Crosbie and Tennenhouse at 1300-1400K. [6] We have also examined the electrode kinetics and transport of 0.5-0.7 μm thick, oxide-free, small, about 0.1 cm^2 , Mo electrodes on K-BASE samples in potassium vapor after holding at $T > 1200\text{K}$ for over 100 hours to remove K_2WO_4 . The porous Mo electrodes demonstrated a non-activated mass transport rate consistent with free molecular flow in porous Mo electrodes, over the temperature range of 900K to 1200K. An activated transport mechanism with low activation energy in acting in parallel with free molecular flow cannot be ruled out, but calculations of free molecular flow rates through the porous electrode adequately account for the observed transport impedance.

Quantitative investigations of Na transport through fairly large area, 14.4 cm^2 , 1.0- 1.2 μm thick $\text{WPt}_{3,5}$ indicated a surface or grain boundary diffusion mechanism, although transport rates were high, not activated from 950K to 1150K, and dominated by the free molecular flow limits imposed by the heat shield. In this temperature range the transport impedance of sodium passing through the electrodes was small compared with the transport impedance calculated for sodium gas diffusing from the exterior of the electrode through the gap between the tube and its

concentric heat shield to reach the external condenser. Transport impedances were low in all cases but were lowest for the electrodes closest to the end of the tube and heat shield. Because these electrodes are not highly porous, but do not hinder sodium transport appreciably, a free-molecular flow mechanism may be ruled out for sodium transport through the electrode. Either a very large pre-exponential factor or a low activation energy for transport via surface or grain boundary diffusion is indicated, but a lower limit may be indicated for the diffusion rate of sodium through these electrodes. A consistent trend is indicated from very slow transport of adsorbed sodium or potassium on Mo or W electrodes; moderate] y facile activated transport of sodium on WRh₂ electrodes; a more rapid activated process on WPt_xMn-contaminated electrodes; and very fast mass transport of sodium on WPt_{3,5} electrodes. The trend suggests more electropositive metals will form less ionic, more covalent bonds with surface adsorbed alkali metals, and that localized bonding hinders facile transport.

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