APPLICATION OF A FUNDAMENTAL MODEL OF THE EXCHANGE CURRENT TO PERFORMANCE OF TITANIUM NITRIDE , RHODIUM-TUNGSTEN , AND MOLYBDENUM ELECTRODES IN THE ALKALI METAL THERMAL-TO-ELECTRIC CONVERTER

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Abstract

AMTEC cells are under development as power sources for future outer planetary robotic space missions, where they must operate for very long times. Mission duration and high temperature operation of AMTECs, to perhaps 1150K at the beta" alumina solid electrolyte (BASE) ceramic, have driven the need to investigate potential degradation reactions of critical components such as the electrodes.

This paper will discuss a comparison of a fundamental model of the exchange current with experimentally derived exchange currents from several electrodes. The high temperature electrochemistry of sodium beta"-alumina ceramics (BASE) with porous metal electrodes has been investigated since the late sixties because of potential applications to thermal to electric energy conversion. The electrochemical reaction occurs at a three phase boundary between the electronically insulating ceramic solid electrolyte, the porous metal electrode, and the gas phase which typically is low pressure sodium gas. The model uses only physical parameters which have been or could be measured by other techniques. The parameters which control the rate and spatial extent of the electrochemical reaction at the three phase interphase region include the morphology of the electrode and solid electrolyte interface; the work function of the sodium coated porous metal surface; the adsorption/desorption rate of sodium atoms from the beta"-alumina surface; the potential energy function of sodium ions bound to the beta"-alumina surface; and the surface diffusion rate of sodium ions on the beta"-alumina spinel block surface. The model is of practical importance because the exchange current may be measured and used to evaluate changes in the electrode/electrolyte morphology with time at elevated temperature, providing information about of slow life limiting processes in high temperature alkali metal thermal to electric energy conversion (AMTEC) cells.

The exchange current has been experimentally evaluated from about 700K to above 1300K for porous molybdenum electrodes and has also been studied in long duration tests of tungsten/rhodium, and titanium nitride electrodes. The exchange current can be extracted from electrochemical impedance spectroscopy and current voltage curves of both power-producing AMTEC cells and sodium exposure test cells (SETC).

Exchange currents of clean molybdenum electrodes decrease slowly with time at temperatures of about 1150-1200K, in experiments running for hundreds of hours, and the decrease is clearly associated with an increase in grain size and a decrease in the length of the three-phase boundary between electrode, solid electrolyte, and the gas phase. Exchange currents of high quality titanium nitride electrodes also decrease, and grain growth is observed at 1173K for 1500 hours. There is little change in the exchange currents for tungsten-rhodium electrodes over 3000 hours at 1173K, but changes do occur in these electrodes which improve their sodium transport properties, and the observed dc exchange rate is dependent on efficient transport of sodium to and away from the reaction zone.

The research described in this paper was performed by the Jet Propulsion Laboratory, California Institute of Technology, and was supported by the National Aeronautics and Space Administration.