Lifetime and Performance of Titanium Nitride Electrodes in AMTEC Cells

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AMTEC, the Alkali Metal Thermal to Electric Converter, is a direct energy conversion device capable of near-Carnot efficiencies; it has been demonstrated to perform at high power densities, with open circuit voltages up to 1.6 V and current densities up to 2,0 A/cm^2 [1-3]. As a power system, AMTEC is expected to deliver 20-25 W/kg. The work described in this paper part of a study to test the suitability of AMTEC power conversion in NASA's X2000 spacecraft program for exploration of the Solar System's outer planets.

Electrodes used in solid electrolyte devices such as high temperature fuel cells and direct conversion devices such AMTEC must meet several criteria for effective operation of the device. At the same time that electrodes must be electrically conducting, they must be thin or porous enough to allow fuel or operating fluid to pass through them. In the absence of pores in the electrode, there must be some other mechanism of transport, such as grain boundary diffusion or ionic conduction through the electrode. In addition, these electrodes are often operated at high temperatures in corrosive atmospheres, so they must be sufficiently refractory to allow operation over long periods.

With a constraint on electrode thickness and the high operating temperature in a sodium vapor atmosphere, electrode materials must be selected with the material's grain growth characteristics in mind. Sputttered or chemically deposited electrodes will form grains during heating and operation; as the electrode material diffuses across itself, grains may grow, ultimately opening voids in the electrode and decreasing the electronic conductivity of the electrode.

Using experimentally determined surface self-difhsioa coefficients, the rate of growth of grains by coalescence may be calculated for temperatures in the AMTEC operating range. There is an inverse relationship between exchange current and grain radius [4]; understanding the rate of grain growth then makes it possible to predict the decline in exchange current over time. Previous work has shown that power produced by an AMTEC electrode is not significantly affected until exchange current declines below 50% of initial exchange current [5]. This relationship then makes it possible to [illegible]

expected to be suitable for very long use at higher temperatures, but are easily degraded by contaminants such as Mn or Ni. This work extends the model to include TiN electrodes, which have been chosen for the present generation of AMTEC cells. TiN electrodes were first repored to have good performance characteristics which were stable over operating times up to 1600 hours by researchers at Ford [7]. The electrochemical behavior of TiN electrodes in AMTEC cells has been reported to show significant differences from that of metallic (i.e. Mo, RhW, PtW) electrodes by researchers at both Kyushu University and at JPL [8,9]. The Kyushu group has studied fabrication of a group of electrodes including nitrides and carbides which have performance characteristics similar to TiN electrodes [9].

In our previous work, we have used the observed grain growth rates to construct a model of electrode life [6]. This model relates grain size to the material's surface Self-diflhsion rate through the Herring scaling law [10]. In addition, the model predicts lifetime based on grain size and the observed relationships among power density, exchange current, electrode resistance (electrical), and electrode integrity.

Titanium nitride electrodes were made by sputter deposition on BASE surfaces. Electrodes which were operated in AMTEC cells or in similar conditions were studied to determine performance over time, including power density, exchange current and resistance. Grain size and electrode composition were also studied after operation. It was found that TiN electrodes have a maturation period of some 200 hours at operating temperature (1100 K), as has been found in other electrode materials [11]. Power density of the electrodes declines in the first few hundred hours, then dots not decline significantly afterwards in cells that have been operated up to 8000 hours [12].

Grain size of TiN electrodes dots not increase rapidly; however, there is some evidence that significant reaction may take place in the electrode. TiN electrodes made by sputtering and operated for 1500 hours at 1013 K were found to have crystals of a Ti/Al nitride phase distributed over the surface, while the TiN grain size had uot increased significantly over the as-sputtered size. TiN electrodes made similarly and operated for 8000 hours at 973 K also did not have significantly increased grain size, but the electrode was considerably thinned. In addition. the electrode operated 8000 hours had incorporated significant quantities of the stainless steel containment materials (Mn, Fe, Cr, Ni).

This paper will discuss the reactions of TiN electrodes in the AMTEC operating atmosphere with reference to time. Previous work has shown that power produced by an AMTEC electrode is not significantly affected until exchange current declines below 50% of initial exchange current [5]. This relationship then makes it possible to predict operating lifetimes for AMTEC electrodes. We have previously used this model to predict operating lifetimes for molybdenum and PtW and RhW electrodes [6]. Mo electrodes appear unsuitable for long term use at T>1125K, while the PtW and especially RhW are

incorporated [illegible] containment materials (Mn, Fe, Cr, Ni).

This paper will discuss the reactions of TiN electrodes in the AMTEC operating atmosphere with reference to lifetime and performance and will present a model of TiN electrode lifetime for AMTEC cells based on the previously developed model