POTASSIUM β"-ALUMINA/POTASSIUM/MOLYBDENUM ELECTROCHEMICAL CELLS

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ABSTRACT

Potassium alkali metal thermal-to-electric converter (K-AMTEC) cells utilizing potassium β"-alumina solid electrolyte (K-BASE) are predicted to have i reproved properties for thermal to electric conversion at somewhat lower temperat ures than sodium AM TECs because of potassium's higher sat urated vapor pressure at lower temperatures. A potassium AMTEC cell was operated, confirming the expected improvement in operation at the rather low temperature of about 7SOK. Potassium vapor electrochemical cells were operated, and the results confirmed the high conductivity of K-BASE ceramic at AM TEC operating temperatures. An i mproved preparation of K-BASE ceramic from sodium β" alumina solid electrolyte (Na-BASE) ceramic resulted in a stronger ceramic and high temperature conductivity close to that of Na-BASE. The conductivity of samples of K-BASE prepared by two methods were compared with respect to temperat ure and t ime dependence following exposure to 1.0 Pa potassium pressure at 1200 K for 500 hours. This test procedure is an accelerated life test of the. electrolyte, since K-BASE may be expected to be used at 900-1100 K range for K-AMTECs. The results show a short period of conductivity decrease, followed by a very slow increase in conductivity. Measurements were performed at intermediate temperatures below 1100 K over the course of a 2500 hour test. Measurements up to 1370 K were carried out rapidly, with the highest temperature maintained for only several minutes. Rapid potassium diffusion on clean Mo surfaces at T > 700K is indicated by limiting currents from electrochemical measurements.

INTRODUCTION AND BACKGROUND

The principal technical hurdle to development of a potassium-based alkali metal thermal-to-electric convert er (K -AMTEC) capable of producing hi@ power density while maintaining an acceptable high conversion efficiency is a high quality potassium β"-alumina solid electrolyte. ceramic (K-BASE). We have conducted an invest igat ion in order to prepare dense K-BASE ceramic and evaluate its ionic conductivity, electrochemical behavior, thermochemical propert ies, and mechanical propert ies, and to demonst rate operat ion of a potassium AMTEC. This paper presents ionic conductivity and electrochemistry of K-BASE with improved strength and reduced porosity, and reports a K-AMTEC test.

The principles of AMTEC device operation in general have been discussed in detail, especially with respect to cell electrochemistry and basic systems modeling.[1-8] Potassium has been shown to provide. a significant advantage over sodium in AMTEC power conversion devices as potassium has a higher vapor pressure compared with sodium. Sodium is the working fluid in AMTEC systems currently being operated and developed.'9 [11]

Potassium is expected to give superior performance in AMTECs below about 1100K and to be the only viable working fluid in AMTECs for which high efficiency operat ion at temperatures bet ween 900K and 1000K is required. The variation of the ratio of the vapor pressures of K to Na varies from about 70 at 373 K to about 2.5 at 1200 K. Transport 1osscs in AMTEC cells are due to pressure gradients which are proportional to the cell's current densit y. These pressure drops arc added to the. condenser pressure, increasing the cold side pressure., reducing the cell's Nernst voltage, which is proportional to log of the pressure ratio across the I] SE. 'J'he model for kinetics in AMTEC electrodes indicates that exchange currents for K should be greater than those for Na by the square root of the ratio of their vapor pressures.[8] 'I'he ionic conductivity of K-BASE up to 1230K is close to that of Na-BASE.[12]

Potassium β"-alumina is a thermodynamically stable phase at the temperatures at which a potassium AMTEC would be most useful (800K to 11 00K).[13,14] 1 lowever, the upper temperat ure stabil it y range is not known, but is generall y thought to be lower than that of sodium β"-alumina, especially by comparison with the stabili zed forms of the latter which include Li + or various small divalent cations such as Mg^{2+} incorporated into the. "spinel block" of the crystal structure in order to stabilize the structure. Most work with potassium aluminate phases has investigated the simpler ternary K-Al-O$_s$ and little work on spinel block stabilized materials has been reported. 1 'he temperature regime at which potassium beta"-alumina becomes unstable with respect to loss of K_2O is within the range of temperatures (1400K to 2000K) at which more traditional ceramic forming processes would otherwise be ut ilized for a material as refractory as K-BASE, however K_2O loss may only reflect instability at low K_2O activity levels.

EXPERIMENTAL

K-BASE with improved ionic conductivity and greater mechanical strength was prepared by ion exchange from lithium stabilized sodium β''-alumina solid electrolyte ceramic (Na-BASE) obtained from Cerametec. The exchange technique was a modificat ion of that of Crosbie and Tennenhouse. They exchanged K" for Na^{+} using KCl vapor at about 1413K without fracturing the ceramic.[13] The K_2O activity was maintained by surrounding the sample with K-BASE powder, and carrying out the exchange under air with potassium chloride vapor at temperatures up to 1625K. This method for preparation of dense, strong, single phase K-BASE was used to exchange a 29.4 cm long. Na-BASE tube and tube sections by KCl exchange at a temperature of 1600K under K-BASE powder in air atmosphere. Dimensional and mass changes were characterized and were consistent with full exchange of potassium for sodium. Samples were also prepared by Crosbie and Tennenhouse's technique for comparison.

K-BASE powders were prepared either from aqueous polymeric oxalates of K, Mg, and Al; or from hydrated oxides obtained by hydrolysis of organic solutions of the three metal alkoxides.[15-17] Fine precursor powders were converted to K-BASE by heating to 1325K. K-BASE were also made. from mixtures of $KAlO_2$, $MgAl_2O_4$, and Al_2O_3 heated for brief periods at 1875K <T< 1975 K.[18]

]iectrochemical characterization was carried out using two and four electrode measurements of samples in potassium vapor in order to characterize the ionic conductivity of the K-BASE electrolyte. Two probe measurements were carried out in a potassium vapor test cell, to characterize the clcctmdc/electrolyte kinetics and K transport through the porous Mo electrode. In that test potassium pressure was controlled separately from tbc test sample by an independent heater. Two samples of solid electrolyte ceramic are held in a high temperature zone, and are contacted by four leads to at least four thin film electrodes. The temperat ures of both the samples of the electrolyte as well as the liquid metal reservoir are monitored by shielded thermocouples.

RESULTS AND DISCUSSION

'The. test results confirm that the ceramic can be exchanged and stabilized with respect to K_2O loss by the KCl exchange at temperatures up to at least 1625 K. An air atmosphere helped inhibit mass loss from the ceramic during exchange. Higher ceramic conductivit y, microcracking of the. ceramic, and K_2O loss competing with exchange have apparently been eliminated. 1 mproved conductivity ics in the K-BASE ceramic also are confirmed. Two exchanges were generally required for a complete or very close to complete exchange, characterized by a >4 % mass increase and a linear expansion of about 1 %.

When K+ for Na" exchange takes place in β''-alumina ceramics, the result is an increase in the c/a ratio of the lattice constants and resultant stresses and microfractures within the ceramic body. When the ion exchange, is carried out at sufficiently high temperature to enable creep in the ceramic to compensate for stresses generated during exchange, the reaction must also be performed under controlled K_2O activity to prevent its loss from tbc ceramic. 'I'he failure strengths of small rectangular ceramic K-BASE and Na-BASE sections and rings were measured. Our results agree well with Crosbie and Tennenhouse's results for similar samples, except that our measurement technique for very small samples gave larger scatter, The new preparation technique yields a K-BASE ceramic which is significantly stronger than that prepared by KCl vapor exchange at lower temperature, and in some cases stronger than the Na-BASE starting material.

Scanning Electron Microscopy (SEM), Energy Dispersive Analysis (EDS), and X-Ray Diffraction (XRD) were used to analyze K-BASE samples. These techniques confirmed the chemical composition and indicated that K-BASE ceramics prepared by both KCl exchange techniques were composed of a β'' phase without detectable β phase. K-BASE powders were found to be mixtures of potassium β''- and β- alumina with K/Al ratios as high as 1 /3, by SEM-EDS and XRD. Sodium and potassium β/β'' phases with Na/Al and K/Al ratios as high as 1/3 have been reported as ternary phases, without stabilizing ions, prepared by decomposition of alkali ammonium tris(oxalato) aluminate precursors at temperatures as low as 1325 K by Takahashi and co-workers [16,17], with the sodium material consisting of major fractions of both β and β'' crystal phases, while the potassium material consisted of predominately the β crystal phase with traces of the β'' crystal phase, Crystal morphology observed via SEM could be correlated with the phases present by XRD and the composition by EDS. The phase purity of β''/β mixtures was evaluated on the basis of several moderate to strong XRD peaks of each phase which are weak or absent in the diffraction patterns of the other phase, discussed by Schmid.[19]

Ionic Conductivity

A tube section prepared by KCl exchange under K-BASE powder and air atmosphere at 1625K, and a section prepared at 1325K by KCl exchange in vacuum were each sputter-coated with four Mo electrodes, and used in assembly of a potassium vapor exposure cell to determine the. high temperature conductivity of the

electrolyte from four-probe d .c. and a.c. conductivity measurements in potassium vapor.[20] Ionic. conductivities were measured to > 1300K; the ceramic prepared hy the new technique has a conductivity on the order of 40% higher than that of the ceramic from the old preparative route. Fig. 1 shows three sets of four probe conductivity data taken with the external pair of electrodes serving as current leads and the internal pair as voltage sensing electrodes. No cover gas was used and the potassium pressure was fairly low, so the potassium atom mean free path in the vapor was very large and we did not expect significant perturbation from ohmic behavior with relatively small currents. The response was linear indicating ohmic behavior. Four probe AC impedance taken with the same electrode arrangement was measured at a modulation amplitude of 20 mV, and the low frequency intercept was used to determine the total sample resistance. Excellent agreement was found between AC and DC techniques at higher temperatures, where the vapor test cell is hcst suited to conductivity measurements. The high temperature conductivity data were corrected for cell geomet ry, and arc present ed in Fig. 2. The effect of the improved higher temperature exchange under air and K₂0 rich K-BASE (circles and diamonds) compared with the exchange carried out at about 1470 K in KCl vapor under vacuum is to increase the magnitude of the conductivity and also to increase the apparent activation energy slightly. Fig. 3 shows the variation of conductivity y at 1000K following sample exposures to low pressure potassium vapor at 1200K over a total of 500 hours. Long test lifetime serves to evaluate the stability and t i me dependence, of conductivity of K-BASE at elevated temperature in a potassium vapor environment.
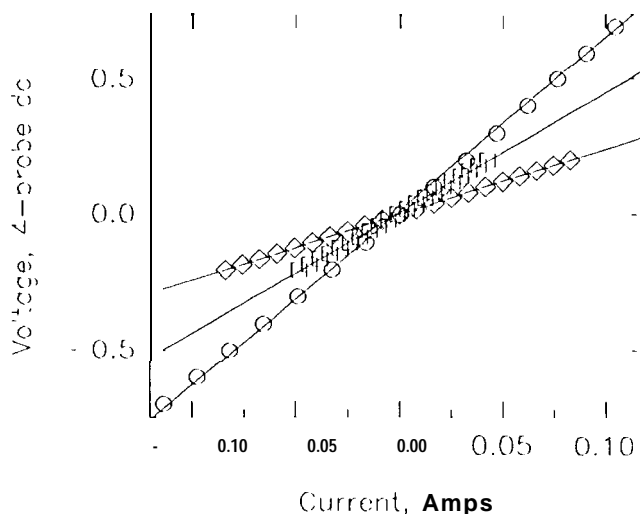

f ig. 1 F our- probe **conductivity** data at 846K, triangles, 6.45 ohms; 1 002K, solid **circles**, 4.41 ohms; 1 307K, open circles, 2.39 ohms
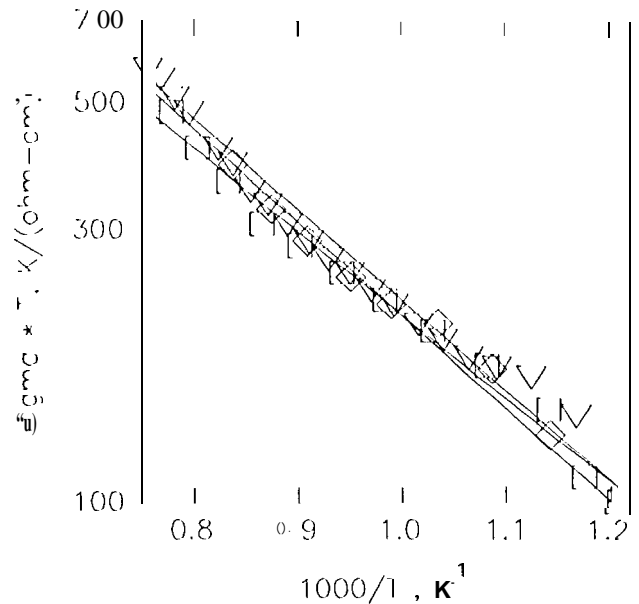

f ig. 2 Conductivity of **K-** BASE **(1 625 K)** after 50,120, and **300"** hours, triangles, squares, and **diamonds,** respectively.
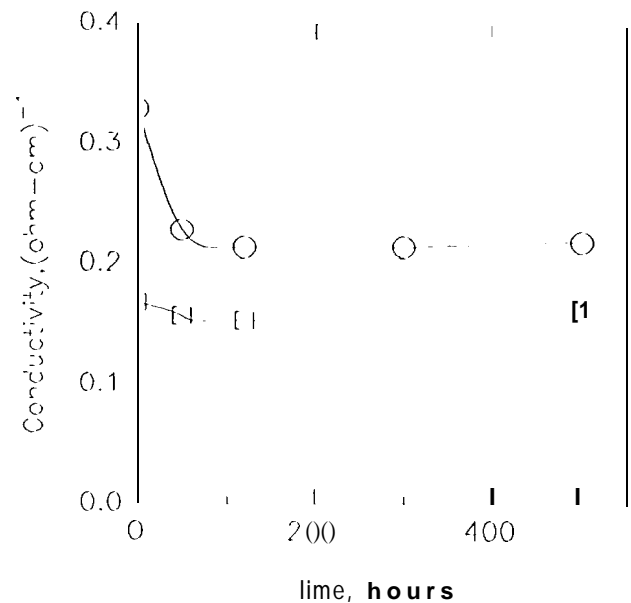

f ig. 3 Ionic conductivity of K- BASE prepared at 1625 **K** circles, **ond** at 1425 **K,** squares, measured at **10()()K,** as a **function of** time exposed to ci bout 1 .0 Pascal **K**g cit 1200K.

Electrochemical Characteristics

Both kinetics and transport of the potassium vapor/porous Mo electrode/K-BASE cell are. quite fast in the upper operating temperature regime of an AMTEC, making precise measurement of these quant it ics difficult, but suggesting that K-BASE AMTEC devices may have

exceptionally low electrochemical losses. Transport limitations can be evaluated from limiting currents of current -voltage curves. It is important to recognize that the limiting current is exhibited by the anode, which takes in potassium vapor and oxidizes it to potassium ions at the three phase interface between the K-BASE, the Mo electrode, and the low pressure potassium vapor. In an AMTEC cell, transport does not usually give rise to a limiting current as the anode is generally a liquid alkali metal anode which has negligible losses at temperat urcs great er than about 725K.[21] Transport losses do occur for alkali metal vapor flowing out of the cathode, which is the low pressure electrode in an AMTI ;C cell. It is a reasonable assumption that at similar pressures, transport will be equally facile in either direction. One difference is that in an AMTEC cathode, the reaction site is the site of highest alkali metal vapor pressure on the low pressure side of the elect rolyte, while at an anode in a vapor cell, the alkali metal vapor pressure is greater on the exterior than at the reaction site. If alkali diffusion is activated and its rate depends, for example, on surface. coverage, the two cases will give different transport losses. Surface transport of K atoms on the Mo electrode is implicated, and is expected to be somewhat faster for potassium than for sodium on mol ybdenum.[22-25] At lower electrode temperatures, the limiting current region is reached at low volts.gcs, and current increases linearly with a greatly reduced slope. Because higher voltages could not be used, as discussed below, current-voltage curves were extrapolated to a current limiting regime at higher voltage assuming the shape of the current voltage curves to be similar, when significant curvature remained near 4.0 V. As a result, the derived values of G and the diffusion coefficient may be expected to be most accurate at lower electrode temperatures. G is a parameter describing electrode porosity, which is zero for electrodes with no resistance to vapor transport. If G is about 100, as found for K on Mo at 900K, acceptable transport losses occur. The best electrodes have values of G below about 20, and may be exploited to give optimal performance in AMTEC cells where other transport losses are not large. Mo electrodes give a value of G = 10 at about 10SOK. Fig. 4 shows the derived diffusion coefficients for potassium diffusion through the electrode. Because the molybdenum electrodes on the improved K-BASE sample were initially about 0.3-0.4 µm thick, they became discontinuous after operation at elevated temperature, as grain size increased to about 1.0 µm diameter. Comparison of the limiting currents with those on the. second sample, which remained cont inuous, suggested that about 4 % of the sample remained electrochemically active. SEM examination indicated that about 1 % of the electrode was cent inuous, apparent ly below the molybdenum screen contacts. Wc calculate the.
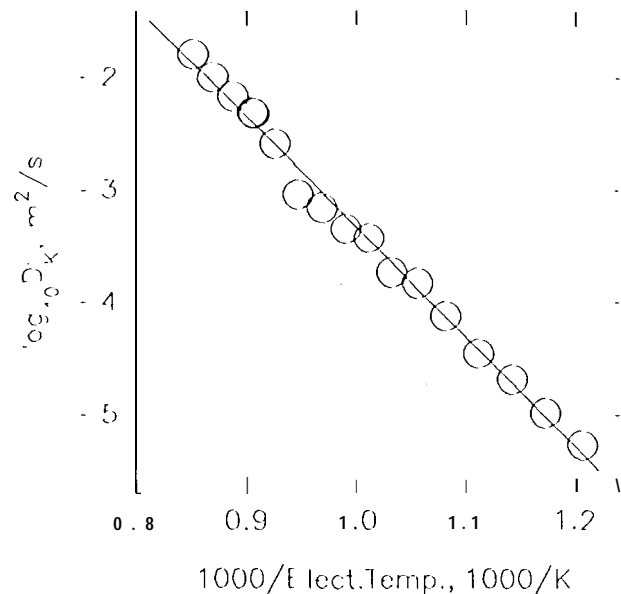

fig, 4 Diffusion Coefficient for **K** on Mo.

diffusion coefficients assuming that the geometric average, 2%, of the electrode is active, with an uncertainty factor of two. Derivation of the diffusion coefficient uses an electrode thickness of $1.0 \mu m$, which is the approximate Mo grain size after several hundred hours at 1200K. The results are expected to depend somewhat on the ambient alkali metal vapor pressure. Average potassium pressures that are very low give anomalously high limiting currents, but the pool exists in a temperature gradient and some wicking to higher tempt.rature regions may occur. Fairly uniform pool temperat urcs were obtained at about 450-475 K; at significantly higher temperatures, the evaporation rate may cause dry out of the hottest region of the liquid potassium pool. Fig. 4 gives diffusion coefficients obtained with a fairly high pool temperatures so that the evaporation rate. will be fairly high, 'but a temperature gradient across the pool of <20 K could be maintained. The result is that we must not ascribe too much accuracy to the absolute values of the derived diffusion coefficients, but we may expect that their temperature dependence, for a potassium pool maintained at nearly constant temperature, should reflect the activation energy of the transport process fairly well.

Voltages higher than about 4.2 V could not be used, because under the experimental conditions of low potassium vapor pressure at high temperature, there is little to hinder excitation of a plasma discharge. Fig. S shows this effect between two nominally isolated leads, with a very small current below 4.0 V and a rapidly increasing current above the ionization potential of atomic. potassium in the vapor, 4.318 V.[26] Fig. 6 shows the current -voltage curve for two electrodes to S.0 V,

with rapid current increase at the potassium ionization potential. This effect is important to applications of series connected AMTECs; in general, series connected cells should not exceed 4.0 V for potassium AMTECs or 5.0 V for sodium AMTECs, unless it can be assured that there are no possible vapor discharge. pathway between cells with potential differences greater than these values.
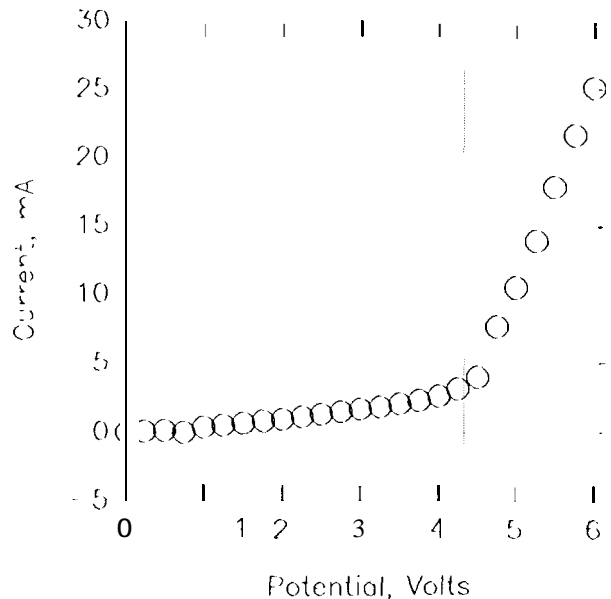

Fig. 5 Current between non-contacted leads in potassium vapor at 992K. Vertical line is at potassium ionization potential = 4.318V
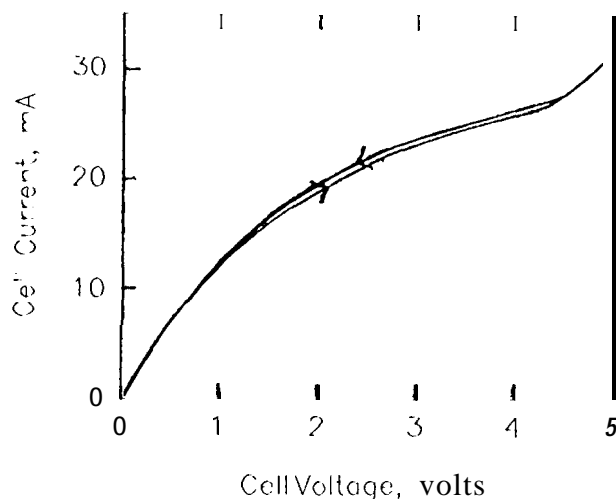

Fig. 6 Curren - voltage curves of two AMTE (electrodes to 5.0 volt S, Increase at V>4.3 is due to plasmad ischarge.

Potassium AMTEC Test

The K-BASE tube, prepared as described above, was successfully brazed to a niobium tube transition, with TiCuNi filler metal, to a small stainless steal flange. The tube was sputtered with molybdenum thin film electrodes for an potassium AMTEC test.

The cell was operated at a nominal temperature of 687 K (at the bottom of the heater well), and one current-voltage curve, shown in Fig. 7, of a 14.4 cm^2 electrode at an estimated temperature of 725-750 K was obtained, with an open circuit voltage of 0.6 volts, short circuit current of 2.5 amps and a total power of 0.3 watts. This performance is modest, but substantially better than the performance of a comparable sodium AMTEC cell at this low temperature. The sodium cell would have a higher open circuit voltage, but current and power densities would be significantly lower at this temperature. However, this was an early-in-life molybdenum electrode, probably containing substantial quantities of K_2MoO_4, which we would expect to be a fairly good ionic conductor at elevated temperature. This phase might persist for viable operation lifetimes at lower cell temperatures, as it is higher melting and slightly less volatile than Na_2MoO_4. Based on the. remits from both AMTEC and vapor cell tests, we would anticipate 1.0 μm thick molybdenum electrodes to be very useful at 900K <1'< 1100K in potassium AMTECs and molybdenum electrodes will not sinter to a diameter exceeding 0.5 μm within periods of years at the lower temperatures.

CONCLUSIONS

Two low temperature mutes to nearly phase pure K-BASE (or Na-BASE) have been demonstrated and characterized. While not directly sintered to dense ceramics except for microscopic areas, this material is useful in ion exchange via ceramic tiring at controlled K20 activity and in potassium metal purification.

We have demonstrated high temperature direct synthesis from aluminates which increases density of K-BASE. This technique could potentially provide high density ceramic with further refinement. Our results generally confirm those. of Schäfer and Weppner, although we did not achieve as high a ceramic density .[18]

Based on improved understanding of the temperature and K_2O stability regime of K-beta "-alumina, the exchange process of Crosbie and Tennenhouse was improved by carrying out the exchange. at a higher temperature, with better control "of K_2O activity. The resulting ceramic shows the appropriate, weight gain of about 4.5 % after exchange, shows only a small anomalous volume expansion (<1 %) over the expected volume expansion due to increase in the lattice

parameters. The new exchange method has several advantages as a route to high quality K-BASE. Any item fabricated from Na-BASE can be exchanged with no loss in strength and no structural distortion other than a linear expansion of ~1 %. Na-BASE ceramic. fabrication is highly developed, so that high quality K-BASE ceramics could readily be fabricated. The 1600K exchange route gives K-BASE with the highest measured ionic conductivity (close to that of Na-BASE), the highest measured failure strength for this material, and the. lowest porosity, and with the phase purity equal to that of the starting Na-BASE. A potassium AMTEC cell constructed using this K-BASE was run briefly with positive results.

The electrochemistry of mature. (oxide free) molybdenum electrodes on K-BASE in a potassium vapor atmosphere has been characterize. For the approximately 1.0 μm thick electrode, held at 1200K for 72 hours to remove K_2MoO_4, potassium transport exhibited an activated diffusion coefficient over 800-1200 K. Interfacial kinetics were fast enough not to be readily separated from the dominating ionic resistance of the electrolyte. These measurements, and the fundamental model for the exchange current in AMTEC electrodes, suggest that exchange currents in potassium cells exceed those in sodium cells.

ACKNOWLEDGMENTS

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