ACTIVATED TRANSPORT IN AMTEC ELECTRODES

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ABSTRACT

Transport of alkali metal atoms through porous cathodes of alkali metal thermal-to-electric converter (AMTEC) cells is responsible for significant, reducible losses in the electrical performance of these cells. Experimental evidence for activated transport of metal atoms at grain surfaces and boundaries within some AMTEC electrodes has been derived from temperature dependent studies as well as from analysis of the detailed frequency dependence of ac impedance results for other electrodes, including thin, mature molybdenum electrodes which exhibit transport dominated by free molecular flow of sodium gas at low frequencies or dc conditions. Activated surface transport will almost always exist in parallel with free molecular flow transport, and the process of alkali atom adsorption/desorption from the electrode surface will invariably be part of the transport process, and possibly a dominant part in some cases. Little can be learned about the detailed mass transport process from the ac impedance or current voltage curves of an electrode at one set of operating parameters, because the transport process includes a number of important physical parameters that are not all uniquely determined by one experiment. The temperature dependence of diffusion coefficient of the alkali metal through the electrode in several cases provides an activation energy and pre-exponential, but at least two activated processes may be operative, and the activation parameters should also be expected to depend on the alkali metal activity gradient that the electrode experiences. Variation in the electrode's physical and morphological parameters, by control during deposition and as morphology evolves with electrode aging, may help to distinguish the influence of activated diffusion from adsorption/ desorption, for example. In the case of Pt/W/Mn electrodes operated for 2500 hours, limiting currents varied with electrode thickness, and the activation parameters could be assigned primarily to the surface/grain boundary diffusion process.

INTRODUCTION

This paper will discuss the microscopic mechanisms which may be operant in electrode kinetics and activated transport; the equivalent circuit description of the physic processes; and finally the specific evidence which can used to evaluate surface diffusion coefficients a chemisorption energies. The interfacial kinetics will also discussed in some detail, as complete resolution of transp processes from charge transfer processes is not possible AMTEC electrode phenomena.

Transport of alkali metal through the poro electrode on the low pressure side of the beta"-alumina so electrolyte (BASE) is a critical process affecting c performance, because a high pressure drop through t electrode significantly reduces the cell's operating volta when current is flowing.[1-3] Several sodium transport mo for different electrodes have been identified or postulate based on experimental results with operating Na AMTI cells. Electrodes containing molybdenum or tungsten oxic before operation in AMTEC cells initially show excelle transport due to ionic conduction of sodium ions throu liquid sodium molybdate or tungstate in the electrod pores.[4] However, Na_2MoO_4 and Na_2WO_4 evaporate elevated temperatures. Ionic conduction is also effective Mo/BASE cermet electrodes, but these have not shown hi power densities reproducibly. The dominant Na transp mechanism in oxide-free Mo and W electrodes has be shown to be free molecular flow diffusion, as transport these AMTEC electrodes shows no activation energy temperatures from 1240 down to at least 900 K.[3] Howev another transport process may be dominant in controlling response of these electrodes in the 1kHz to 10 kHz frequen range. Activated transport via surface diffusion, gr boundary diffusion, or diffusion of alkali metal though electrode's crystal structure may be important in otl instances.[5] The desorption of an alkali metal atom from pore wall or from the exterior surface of an AMTI electrode may also be an activated, rate-limiting transp step in some cases. Surface diffusion is a contributi transport mode in Mo electrodes at kHz frequencies, shown by the Warburg-like frequency response in a impedance measurements.[3] Free molecular flow transp can be calculated to be so rapid through films with the p

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structure of thin Mo electrodes that it would give rise to a purely resistive response below MHz frequencies.[3,6]

Surface diffusion is also likely to provide the dominant Na transport pathway in W/Pt and W/Rh electrodes, which show little open pore area but have excellent Na transport properties at AMTEC operating temperatures from 1100-1200 K.[5] In Na vapor exposure cells, W/Rh and W/Pt electrodes on BASE substrates show activated Na transport, determined from anodic limiting currents, over temperature from 700-1100 K. [7] Experiments run for >1000 hours with W/Pt electrodes have been strongly contaminated with Mn from the steel chamber, heated externally in a furnace, but the resultant electrodes, while not practicable for AMTEC electrodes, have quite good electrochemical characteristics and only slightly increased grain size. This paper will include results from Pt/W/Mn as a model electrode with well defined behavior.

Potassium transport through thin Mo electrodes at lower temperatures (700-900 K) appears to be quite complex mechanistically, while overall kinetics and transport at higher temperatures is very favorable. At the lower temperatures, the current voltage curves are very complex, which is unusual compared with the behavior of sodium at molybdenum electrodes.

These investigations are contributing to optimization of AMTEC electrode performance, involving requirements for long life, efficient mass transport, rapid electrochemical kinetics, and low electrode sheet resistance.

The Mechanistic Model and AC Impedance sections discuss modeling of interfacial kinetics and transport, and are summarized in the Conclusion. New AMTEC experimental results on transport follow the modeling results.

EXPERIMENTAL

The experimental techniques used in electrode characterization in AMTEC cells, in alkali metal vapor exposure test cells, as well as data reduction techniques have been described previously.[2-4,7-9] Vapor exposure cell experiments utilizing Mo electrodes sputter-deposited on potassium beta"alumina solid electrolyte (K-BASE), and W/Pt or W/Rh electrodes deposited on sodium beta"-alumina (Na-BASE) were used to obtain most of the temperature dependent data reported here. Standard expressions for alkali metal vapor pressures were used.[10,11].

RESULTS AND DISCUSSION

The Mechanistic Model: Kinetics

The microscopic model for kinetics and transport in AMTEC electrodes requires understanding of the dependence of electrode operation parameters on electrode and interface morphology, as well as experimental characterization of these parameters with respect to temperature and other variables. This model contains significant simplifications which may be readily apparent, but it begins to put AMTEC electrode mechanistic phenomena at an molecular level on a more quantitative level.

Measurements performed on mature thin (0.5μm) Mo

and (1.0-1.5μm) W/Rh and W/Pt electrodes have show fairly consistent exchange currents which are proportional t collision rates of Na gas at the interface over several hundre K.[3] The transfer coefficient, α, is always determined to b close to 0.5 for high quality impedance data on matur electrodes at high temperatures, T>1100K, and n systematic deviation from this value is observed on coolin; although the scatter in derived values increases substantiall This argues for a simple, one-step, symmetric reaction f Na$^+$ + e$^-$ → Na. The exchange currents of the thin M electrodes decrease somewhat over several hundred hours about 1200K as the grain size increases, and tl Mo/BASE/Na$_G$ contact zone decreases in magnitude. F these high performance electrodes, using data for grain siz void area, and approximate electrode grain/BASE conta angle, the length of the three-phase boundary, L$_3$, estimated to be 3 - 6 x 10^4 cm per cm^2 of project geometric electrode area, A$_{GEOM}$. At zero net current flo approximately one out of each 500 to 2000 collisions whi would occur at a hypothetical planar surface with ar A$_{GEOM}$ results in a reaction to produce sodium ions in tl BASE and electrons in the porous metal electrode. Express another way, a 1.0 cm^2 electrode has an area of 0.002 cr where a sodium atom from the gas phase will be oxidiz 50% of the time it collides; and a sodium ion reaching tl surface will be reduced 50% of the time also, at op circuit. If the entire three phase zone were electrochemical active, it would need to be only ~0.5nm wide. This may n be too great a rate to be caused by simple collisions a electron tunnelling near the three-phase boundar Alternatively, reactants may be rapidly transported to t three phase boundary, or the reaction zone may be greater extent than an atomically narrow zone at the juncture of t BASE with the porous metal and the gas phase. Estimates the macroscopic fractional reactive surface area of a BA! ceramic surface, F$_{EDGE}$ range from 5% to 30% of the to BASE surface area, A$_{BASE}$, which is several times A$_{GE}$ because the ceramic has a bumpy, irregular surface. The estimates are based on low temperature surface decorati experiments, and scanning electron microscopy, for F$_{EDGE}$ a A$_{BASE}$, respectively.[3]

Of crystal surfaces containing defect plane edges, thickness t$_{DEF}$ of the defect planes themselves is a fraction total which also includes spinel block edges with thickn t$_{SPIN}$. Spinel block edges are not expected to capture/evol sodium atoms. The fractional microscopic reactive BA: surface area of the projected surface area, F$_{RCT}$, is estimat

$$F_{RCT} = F_{EDGE} \times A_{BASE} \times t_{DEF}/[A_{GEOM} \times (t_{DEF}+t_{SPIN})] \quad \text{(Eq.}$$

$$F_{RCT} = 0.013 \text{ to } 0.16$$

The corresponding length of the three phase bound; crossing defect plane edges is in the range of 0.04 to 1.0 10^4 cm. The reaction probability, P, for electron tunnelli to a sodium ion at distance a in a defect plane edge described using as a model a simple rectangular poten barrier with a height equal to the electrode's work functi ϕ ≈ 2.5 eV = 4.00x10^{-19} J, for a Mo or W alloy electr covered with a partial monolayer of Na; The electro

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energy is E_e; and the total barrier height is $V = E_e + \phi$. The electron mass is $m_e = 9.11 \times 10^{-31}$ kg; and Planck's constant $h = 6.626 \times 10^{-34}$ J-s. The probability P is given in Eq.2a: [12]

$$P = 16E_e(V-E_e)V^{-2} \exp[-4\pi a(2m_e\phi)^{1/4}/h] \qquad (Eq.2a)$$

If we take T=1000K for convenience, the energy of the tunnelling electron is $E_e \approx kT = 1.38 \times 10^{-20}$ J, where $k = 1.381 \times 10^{-23}$ J/K is Boltzmann's constant; and as a result $V = E_e + \phi \approx 4.14 \times 10^{-19}$ J.

$$P \approx 0.515(\exp[-4\pi a(2m_e\phi)^{1/4}/h]) \qquad (Eq.2b)$$

Tunnelling probabilities at a = 0.5, 1.0, 2.0, 3.0, and 4.0nm are $P = 1.7 \times 10^{-4}$, 1.3×10^{-8}, 5.7×10^{-15}, 1.5×10^{-22}, and 3.3×10^{-29}, respectively. Because the density of valence level electrons and available empty states in the metal is very high, and the Na^+ ion density in BASE is also fairly high, these probabilities along with the reactant/product densities and the observed lack of significant activation energy strongly support the tunneling model and suggest the BASE defect block edge as the reaction site, although they also suggest that the reaction occurs primarily quite close (<1nm) to the three phase contact "line".

Calculation of a reaction rate from Eq. 2a requires that some estimate of the densities of initial and final states involved and the attempt frequency be included. The value of the reaction rate is taken to be the product of the surface concentration of Na^+; an absolute attempt frequency equal to kT/h; and the transmission probability, P, given above.[13]

$$k = d(Na^+) \times (kT/h) \times (.515(\exp[-4\pi a(2m_e\phi)^{1/4}/h])) \qquad (Eq.3)$$

where $d(Na^+)$ is the density of accessible Na+ ions at a distance a from the emitting electrode surface, where the density of electrons of appropriate energy capable of tunnelling is $d(e^-)$. At 1000K, kT/h is equal to 2.084×10^{13} s^{-1}. If for example we wish to calculate the reaction rate of sodium ions between .70 and .90 nm from the three phase line, with electrons between 0.55 and 0.65nm above the three phase line,L_3, assuming an approximate contact angle of electrode with base of 90°, an estimate of the density of Na^+ ions, $d(Na^+)$, is required. The electron density, $d(e^-)$, is estimated from the density of Na atoms adsorbed on the electrode surface, but does not enter the rate equation. The length, L_3, was calculated above to be 3 to 6 $\times 10^4$ cm/cm^2, which multiplied by a height of 1nm, and a surface density of 13.4 nm^{-2} for a monolayer of Na atoms, gives a density at this height in a 1 cm^2 electrode of:

$$d(e^-) \approx 4.0 \text{ to } 8.0 \times 10^{11} \qquad (Eq.4)$$

From L_3, the boundary crossing defect plane edges, $d(Na^+)$ at .7 to .9 nm, in a 1 cm^2 electrode is calculated in Eq.5, and the resulting rate and current density in Eq.6a and 6b :

$$d(Na^+) \approx 0.04 \text{ to } 1.0 \times 10^{11} \text{ atoms/}cm^2 \qquad (Eq.5)$$

$$k = 0.11 \text{ to } 2.7 \times 10^{20} \text{ atoms/}(m^2\text{-s}) \qquad (Eq.6a)$$

or: $j = 1.8$ to 43 Amps/m^2 $\qquad$ (Eq.6b)

A similar calculation for a=.4 to .6 nm give contributions to the reaction rate of k=.14 to 3.5×10 atoms/m^2, and to the exchange current of j= .23 to 5.6×10 Amps/m^2 an increase of nearly 10^4. These estimates may b somewhat misleading: the first only "counts" one segment c the electrode wall and most of the Na^+ ions will be reduce by the nearest section of the electrode; the calculated rat was too small; the second ignores the other losses in th process which may impede ion resupply to a small favore reaction area element. However, these calculations show th observed exchange currents in real electrodes, typically abo 1×10^5 Amps/m^2, are quite consistent with calculations of th reaction rates and exchange currents based on known, imprecise, electrode and electrolyte properties. Th calculations also show the steepness in dropoff of reactio rate away from the hypothetical three phase line. It possible that there may be a minimum approach distance, c the order of perhaps 0.2 to 0.5nm, which occurs in th actual system. However it is also possible that som asymmetry exists for this reaction even though not reflecte in an clear deviation of the transfer coefficient, α, from value of 0.5. Reduction of Na^+ may occur under th electrode grains to some extent, and while Na^+ would t expected to be absent, or strongly bound on BASE surfac away from the defect block, Na atoms may diffuse on BAS to the reaction zone.

There is, of course, a weak temperature depende increase in the collision frequency of Na gas with th interface and presumably, Na^+ ion arrival rates at th reaction zone in the BASE, which can be considered as thermally activated attempt rate, as well as the we temperature dependence of the tunnelling probability due the increases in E_e with temperature.

A somewhat fuzzy experimental upper limit on tl extent of the reaction zone can also be established, since tl sintering of thin Mo electrodes at ~1200K leads eventually a drop in the observed exchange current after the Mo gra size has reached approximately 0.6 to 1.0 μm and holes the Mo film of 1.0 to 5.0 μm appear. Therefore we c expect that the upper limit of the extent of the reaction zo is less than 1.0 μm and the lower limit is on the order of about 1.0 nm. The upper limit distances are beyond tl expected range of electron tunnelling, although a hoppii mechanism could be used to explain a long range $e^-/Na^+/\Gamma$ reaction if it is ever observed. However, for completene alternative mechanisms will be briefly discussed. Oth potential mechanisms involve thermionic emission electrons from the metal surface followed by Na^+ ion captu of electrons which "stick" to the BASE surface; or Na^+ i evaporation from the BASE surface to the metal. Gas pha reaction of Na^+ ions with electrons supplied by thermior emission or tunnelling need only be considered if Na^+ i evaporation has a high rate. The Richardson equation f thermionic emission is:[14]

$$j_e = AT\exp(-\phi/kT) \qquad (Eq.$$

A is a constant and j_e is the emission current

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Amp/cm^2. The value of the exponential term at 1000K is 2.6x10^{-13}, so that unless A is exceedingly large, thermionic emission, while not completely negligible in magnitude, would give rise to a electrochemical rate which would be strongly activated, and smaller in magnitude than tunneling.

Similarly, the rate, or flux, of escape of Na$^+$ ions from the BASE surface, k_{Na}^+, or j_{Na}^+, is expected to be a strongly activated process, and the equilibrium vapor pressure of Na$^+$ ions above BASE at typical AMTEC operating temperatures will be low.

$$k_{Na}^+ \leq (F_{RCT})[d(Na^+)](kT/h)[exp(-E_I/kT)] \qquad (Eq.8a)$$

$$k_{Na}^+ \leq .17 \text{ to } 2.1x10^{14} \text{ atoms/cm}^2\text{-s} \qquad (Eq.8b)$$

$$j_{Na}^+ \leq .27 \text{ to } 3.4 \text{ x}10^{-1} \text{ Amps/m}^2 \qquad (Eq.8c)$$

The first two terms in this expression give the total number of Na$^+$ ions on the BASE surface; the third term is the absolute evaporation attempt frequency at T=1000K.[13] The exponential gives the probability of the energy of Na$^+$ ions necessary for vaporization from the BASE surface, E_I≈2.64eV, which is approximately the ionization potential of a free Na atom, IP =5.139 eV, minus the work function, ɸ ≈ 2.5eV, because there is no electron produced in the gas phase. Additional activation energy may be involved, but clearly the ion evaporation step is highly temperature dependent and activated, in spite of the favorable supply of Na$^+$ ions on the BASE surface; any mechanism requiring evaporation of Na$^+$ ions cannot account for the large exchange currents observed at AMTEC electrode.

The Mechanistic Model: Transport

The transport mechanism when surface or grain boundary activated transport occurs will be quite complex. In nearly all cases, some level of gas phase transport will occur in parallel with, for example, surface diffusion, and adsorption/ desorption will connect the two transport modes. Adsorption may be a necessary step at the interfacial region if, as we suggest, the Na atom is not produced on the metal surface. Desorption at the exterior surface of the electrode is a necessary step in dc operation of an AMTEC cell. Adsorption and desorption will occur between the parallel gas and surface-confined transport routes, with the net effect of bringing the alkali activity in the gas phase closer to the surface activity. Calculations utilizing reasonable surface diffusion rates and desorption activation energies may be used to estimate how close the activities of surface and gas-phase alkali are to equilibrium. Both the surface binding energy and the surface diffusion coefficient are typically strong functions of surface coverage, when coverage is less than one monolayer.

If an isolated electrode grain edge on a BASE surface is considered, for example at the periphery of an electrode, we may do an approximate calculation of the distance an alkali atom will travel on the surface before desorbing. Because this edge effectively borders an infinitely wide pore, the Na pressure in the gas phase due to Knudsen flow alone will drop precipitously as the interfacial region is left behind. Ideally, the adsorption isotherm, or fractiona coverage with alkali metal atoms, ɵ, is known or can be estimated; as well as the rate of evaporation, and the surface diffusion rate, $D_S(ɵ)$, as a function of coverage, ɵ. Some information is available for Na and K on Mo and W surfaces.[15,16,17] Little of the required information is known about Na surface adsorbed layers on AMTEC electrodes such as W/Rh or W/Pt. If a Langmuir isotherm i assumed, with adsorption energy independent of coverage coverage drops off exponentially moving away from th interface:

$$V_D = K_D ɵ \exp[-E_D/RT] \qquad (Eq.9$$

where V_D is the rate of desorption, K_D is a constant, and E is the activation energy for desorption. If a Temkin isotherm is assumed as in ref.[3], with estimated binding energy decreasing with increasing with coverage from 234 kJ/mol at zero coverage to 96 kJ/mole at full coverage, the rate o desorption will fall off more slowly with distance because th binding energy will increase as coverage decreases. [16,17 We take n = n_S ɵ, in atoms cm^{-2} where n_S is the tota number of surface sites per unit area are occupied by monolayer of Na, and n=n_0 at z=0 , and D_S is the surfac diffusion coefficient of Na on the surface. At a unit are element at a distance z from the interface, the difference i the surface arrival and departure numbers of atoms $D_S d^2n/d$ of surface diffusing Na atoms is equal to the evaporatio rate per unit area, V_D, expressed in atoms s^{-1} cm^{-2}:

$$V_D = D_S d^2n/dz^2 = n[kT/h]\exp[-E_D/RT] \qquad (Eq.1($$

where K_D ɵ has been replaced in Eq.9 with the density c states, n, multiplied by the attempt frequency, kT/h. Eq.1 can be solved to give:

$$n(z) = n_0\exp\{-[kT/hD_S]\exp([-E_D/RT]^{0.5}z)\} \qquad (Eq.11$$

Assuming a typical value of $D_S = 10^{-8}m^2s^{-1}$ and an activatio energy E_D of 160kJ/mole, at 1000K, then at z = 0.5 μm an 1.0 μm, n will equal .22 n_0 and .048 n_0, respectively showing that desorption occurs rapidly as the Na atom move away from the interface. In a more realistic physical mode the grain wall will bound a crevice, and the gas phas pressure will be more nearly in equilibrium with th absorbed species until the top of the grain is reache Desorption occurs readily for a typical grain size of 1.0 μn

AC Impedance Results

Impedance results on all AMTEC electrodes invariably gi an increasing value of the capacitance as frequency decreas if individual frequency data sets are fit to a parallel R circuit. The calculated capacitance sometimes reaches a near constant value at frequencies around 10 kHz, but invariab rises steeply at low frequencies. The circuit may be fit wi a constant phase element or equivalently with a generaliz capacitance, but such fits, while helpful in obtaining valu of the resistive components, series inductance, ar occasionally the interfacial capacitance when it can l

resolved at higher frequencies, do not shed any light on the nature of the capacitive contribution to the transport process. A finite Warburg impedance was anticipated for a surface diffusion transport path, and shown to act as a purely resistive component for free molecular flow gas diffusion at frequencies below 1MHz. Only thin mature Mo electrodes have provided ac impedance data of sufficient quality for resolution of a well defined finite Warburg element, which was somewhat flattened at low frequencies.[3] Good quality WRh_2 to WRh_3 composition electrodes have shown rather similar features. Resolution of a finite Warburg element after subtraction of series resistance and inductance, followed by subtraction of the parallel interfacial capacitance, and finally the generalized charge-transfer resistance in series with the transport impedance is not alone sufficient to define transport parameters. This is because a finite Warburg impedance in parallel with the resistive network due to free molecular flow diffusion and gas/surface exchange behaves exactly like a finite Warburg with altered characteristics. Initial and terminal resistive processes affect the high frequency series resistance, but under ideal conditions, a physical process described by two parameters for surface diffusion and surface coverage, a adsorption/desorption energy for exchange between gas and surface atoms, a resistance for gas phase diffusion, and initial and final resistances for adsorption and desorption, will give rise to an equivalent circuit characterized fully by only three parameters instead of six. Additional information may be obtained by morphology studies, activation energy determination from temperature variation, and variation in electrode thickness to resolve activated surface transport from adsorption/desorption.

Temperature and Morphology Dependence of Transport of Na on Mo, WRh, WPtMn; and K on Mo

The transport behavior of Na on thin, mature Mo electrodes has been most thoroughly studied by ac impedance and current-voltage curves over a wide temperature range, 740K to 1240K, in AMTEC cells with small area electrodes. Typically ac impedance was used with $1cm^2$ electrodes and current-voltage curves of 4 to 10 cm^2 electrodes were fit with the transfer coefficient constrained at 0.5 to the general kinetics/transport model to give values of the exchange current and a dimensionless transport parameter, G, which could be associated with the electrode's pore structure determined by scanning electron microscopy in the case of electrodes with free molecular flow dominated transport.[2,3,9] G could be related directly to a diffusion coefficient for Na gas passing through the electrode, D_{Na}; neither parameter showed strong temperature dependence, with G about constant and D_{Na} decreasing slightly with increasing temperature, consistent with free molecular flow. Several WRh_2 electrodes were similarly characterized in AMTEC small electrode cells at temperatures from 900K to 1200K. The values of D_{Na} increased rapidly with temperature at around 1000K, and the process was somewhat reversible, with slight changes in performance after temperature cycling. WRh_2 electrodes were characterized extensively in a sodium exposure test cell (SETC) where a section of BASE tube with several electrodes could be

maintained in Na gas at typical AMTEC operating temperatures for several thousand hours. Limiting current from current voltage curves were used to determine values o D_{Na} over a range of electrode temperatures and Na pressures The diffusion coefficients normalized for thickness wer determined over a range from 725K to 1150K, at N pressures near 4 Pa:

$$D_{Na} = 4.56 \times 10^{-3} exp[-43.5kJ/RT] \ m^2 s^{-1} \qquad (Eq.12$$

correcting for the estimated length of the crevice walls i WRh_2 in these electrodes :

$$D_{s,Na} = 4.56 \times 10^{-7} exp[-43.5kJ/RT] \ m^2 s^{-1} \qquad (Eq.1:$$

Several SETC experiments were also performed with W/I electrodes; however, the temperature cycling experimen were performed late in test when Mn contamination of the: electrodes had become severe. The temperature depende transport data for these electrodes probably is representativ of Na transport on MnPt, a dominant phase aft contamination. Electrode performance did not degra severely however, and MnPt might be a rather goc electrode for lower temperature applications if the surfa diffusion coefficient of Mn on the electrode were small. F 1-2.5 μm thick MnPt/W electrodes, in approximately 10 l Na_s, the diffusion coefficients normalized for thickness we determined over a range from 765K to 1175K:

$$D_{Na} = 0.855 exp[-172kJ/RT] \ m^2 s^{-1} \qquad (Eq.1$$

correcting for the length of the three phase line:

$$D_s = 2.85 \times 10^{-5} exp[-172kJ/RT] \ m^2 s^{-1} \qquad (Eq.1$$

In the cases of both WRh_2 and MnPt/W, the surfa diffusion measurements were analyzed for limiting curre data measured at similar ambient Na vapor pressures, ratl than at constant surface coverage, since the correct isotheri are not known. Therefore the surface diffusion expressic have not been deconvoluted from adsorption effects.

The electrochemistry of Mo electrodes on potassii β''-alumina (K⁺BASE) in a K vapor atmosphere has a been investigated. Only four-probe conductivity measureme and current-voltage curves were taken after the electrodes I matured for about 120 hours at >1200K. Current-volt: curves did not show well defined limiting currents temperatures from 910 to 1210K, but lower limits diffusion coefficients for K within these electrodes could determined from current maxima. There was no system: temperature dependence of D_K; the smallest value measu was 4.78x10-5 $m^2 s^{-1}$ at 1105K, and the largest was 1.01x ^{4} $m^2 s^{-1}$ at 1058K, and intermediate values of D_K w measuremed at 909K, 941K, 1106K, and 1207K. Th results suggest that porous Mo electrodes on K⁺BASE ir vapor are efficient free molecular flow electrodes compar: to the same electrodes on Na⁺BASE in Na vapor. A par: enhancing activated transport mode may exist but does seem to dominate in these electrodes. Current-voltage cur showed a distinct local minimum in slope, dj/dV, at 0V

T<900, an unusual feature for alkali vapor cell experiments.

CONCLUSIONS

The temperature dependence of Na transport in WRh[2] AMTEC electrodes first indicated an activated transport mode, and the favorable high temperature Na transport in W/Rh and W/Pt electrodes having low porosity electrodes suggested surface diffusion or grain boundary diffusion significantly augmented gas phase diffusion in these electrodes. Given the experimental observation that the interfacial reaction rate is not activated, and can be accounted for by a reaction zone near the three-phase interface line, the most likely mechanism is electron tunnelling from the electrode to a Na^+ ion at the surface of the beta"-alumina, which involves tunnelling through a barrier equal to the work function of the electrode surface (~2.5eV) with a barrier thickness of ≤ 1.0 nm. The alkali metal atom is therefore produced on the BASE surface and may travel by gas phase diffusion or chemisorb on the metallic electrode and move by activated surface or grain-boundary diffusion. While gas phase diffusion has been found to dominate transport of Na through thin, mature Mo electrodes, and the observed diffusion coefficient for Na in these electrodes is not activated, ac impedance measurements have clearly indicated a parallel, slower transport mode which dominates electrode performance at higher frequencies, and may be activated. Alkali metal vapor exposure cell experiments have allowed long term investigations of the electrochemical responses of WRh_2 and W/Pt/Mn electrodes in a Na atmosphere and Mo electrodes on K-BASE in a K atmosphere. Activation energies which appear to be associated with the transport process were measured for the WRh_2 and W/Pt/Mn electrodes. Approximate expressions for surface diffusion rates were obtained from these data with knowledge of electrode morphology. Neither current voltage curves nor ac impedance data taken for a single set of electrode parameters: temperature, thickness, grain size, ambient alkali metal vapor pressure, etc, will allow resolution of all the important mechanistic processes occurring in mass transport coupled to charge transfer. By varying these electrode and operating parameters, more features of the electrodes' mechanisms may be resolved.

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