A QUANTITATIVE MODEL FOR THE EXCHANGE CURRENT OF POROUS MOLYBDENUM ELECTRODES ON SODIUM BETA"-ALUMINA IN SODIUM VAPOR

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ABSTRACT

This paper presents a model of the exchange current developed for porous molybdenum electrodes on sodium beta"-alumina ceramics in low pressure sodium vapor, but which has general applicability to gas/porous metal electrodes on solid electrolytes. The exchange current is first defined to be consistent with the quantity measured in dc electrochemical experiments; we make a distinction between the dc electrochemical exchange current and an ac electrochemical exchange current measured at about 103 to 104 Hz. We also distinguish the electrochemical exchange process from a chemical sodium exchange process between the solid electrolyte and the sodium vapor which does not involve the electrode. 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.

This model for the exchange current in a gas/solid electrolyte/porous metal electrode system, including all steps but the last, which has not been measured, gives excellent agreement with experiment from about 700K to 1000K and the discrepancy at 1000K to 1300K permits estimate of the activated sodium diffusion rate on the 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 slow life limiting processes in high temperature alkali metal thermal to electric energy conversion (AMTEC) cells.

INTRODUCTION

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.[1] 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.[1-3]
The exchange current has been experimentally evaluated from about 700K to above 1300K for porous molybdenum electrodes and has also been determined for tungsten, tungsten-rhodium, tungsten-platinum, sodium molybdate-molybdenum, and titanium nitride electrodes over more restricted temperature ranges.[2-5] The extraction of the exchange current from impedance data and current voltage curves of AMTEC cells have also been described.[2] A number of other investigations of electrode performance have reported high performance AMTEC electrode characteristics which indicate high exchange currents and favorable mass transport.[6-9] An incomplete model of the exchange current has been reported, and this paper adds to that model.[10]

The calculations used in development of this model involve accepted treatments and equations, and the mathematical steps have been discussed in a previous publication.[10] These are discussed very briefly below and referenced.

DEFINITION AND DESCRIPTION OF THE EXPERIMENTAL EXCHANGE CURRENT IN THE THREE PHASE SYSTEM

The general definition of the exchange current is that it is the balanced faradaic activity equal to current of either sign at rest potential.[11] Its value may also be defined, consistent with rate theory, as a quantity in the electrochemical current-overpotential equation which fits the observed current flow in the cell when the voltage is perturbed from the open circuit value.[11]

The electrochemical exchange current in the three phase system may also be defined, in accordance with experiment, to be the exchange current derived from the dependence of small currents in the electrochemical cell on small voltage perturbations from the steady state.

In region A, part of the three phase interface is contained within a cavity which does not communicate with the electrode exterior. A net Faradaic current may flow when the electrode's potential is changed, but will cease when the sodium activity in the cavity reaches an appropriate level. Measurements of the exchange current using moderate ac frequencies will include a contribution from Faradaic reactions in such cavities, but there will be no contribution to the dc exchange current. In most of the measurements of the exchange current of Na(g)/porous Mo/BASE, higher frequency measurements are used primarily to separate ohmic resistances of the electronic conducting electrodes and leads and ionic resistance of the BASE from the electrochemical resistances due to charge transfer and mass transport. The mass transport process has a large pseudo-capacitive component, and the double layer capacitance is in parallel with the total Faradaic resistance. Therefore the electrochemical processes do not contribute greatly to impedance at frequencies above about 104-105 Hz. Detailed fits to impedance spectra at 103-104 Hz allow derivation of an ac exchange current about three times higher than the dc exchange current.[3]

In region B, vibrationally excited sodium ions on the defect block surface can accept electrons from sodium atoms adsorbed from the gas phase. This exchange requires no electrode; it does not contribute to electrically measured electro-chemistry; is expected to be exceedingly fast at the temperatures and sodium pressures under consideration; and would be most easily measured by isotope exchange studies. Because both the electrochemical exchange process and the much more rapid chemical exchange process occur simultaneously, it is probably impossible to obtain the electrochemical exchange current from an experiment at zero current.

In region C, neutral sodium produced at the three phase interface has access to the electrode exterior. Electrons may tunnel from these sodium atoms to appropriately reorganized sodium ions near them on the defect block edge. This process may occur a large number of times before
Reaction sites under grains do not contribute to dc exchange current.

Chemical exchange at BASE surface does not affect exchange current.

Desorption of a sodium atom and constitutes a random walk of the electron along the defect block edge.

The top view in D shows the different components of the electrolyte surface which contribute to the rate of the electrochemical exchange; the processes which are critical to allowing the reaction in each of these areas are indicated.
SUMMARY OF CALCULATIONS

Sodium ion diffusion from the bulk to the surface of the defect block is estimated to be not much larger than the activation energy for ion diffusion in the bulk, because Na(liq)/BASE/Na(liq) cells show only ohmic resistance above about 723 to 773K.[12-14]

Electron tunneling from the electrode to a vibrationally excited Na' is calculated assuming transmission through a rectangular barrier of height equal to the work function (2.5 eV) of a Mo or W electrode coated with Na or K, with coverage between about 0.3 and 1.0 monolayer.[15-22] For a Na' on the BASE surface, the tunneling rate is numerically integrated over the electrode surface in cylindrical coordinates.[10]

The attempt frequency for tunneling is calculated from the collision frequency of conduction electrons within k(B)T of the Fermi level with the electrode surface, treating Mo as a free electron metal with 6e-/atom, and noting that free electron metal parameters such as density of states at the Fermi level and low temperature heat capacity are within a factor of two of measured values or values from more detailed calculations.[23,24]

The probability that a surface bound sodium ion is in one of a number of suitably vibrationally excited for conversion to a sodium atom (which has a diameter greater than the ion by 0.09 nm) by tunneling is calculated assuming a Boltzman distribution of excited states with energy differences like those of a harmonic oscillator. The potential energy diagram for the ion on the BASE surface is estimated from the binding energy, the ionic radii, and the assumption of electrostatic attraction and Pauli repulsion.[25-27] This is consistent with the general assumption that atomic rearrangement must precede high probability tunneling to a low energy state.[28]

The adsorption/desorption rate of sodium atoms from the beta'-alumina surface is calculable from the kinetic theory of gases and vapor pressure of sodium with the assumption of moderately weak binding and moderately high sodium activity.[29,30] Sodium atom binding energy to BASE is estimated to be similar in magnitude to Na atom binding to bulk sodium, on the basis of liquid sodium wetting of BASE, the interfacial resistance of Na(liq)/BASE/Na(liq) cells, a binding energy calculation, and thermodynamic data for sodium.[10,14,29,31]

Sodium ion binding energies on the surface of BASE are taken from thermal desorption measurements.[25] The activation energy and displacement necessary for Na' diffusion on beta'-alumina may be estimated, and could be measured on model surfaces. The surface diffusion rate of sodium ions on the beta'-alumina spinel block surface has not been measured, but the binding energies suggest that it is too slow to be important except at higher temperatures.[25] The binding, activation, and diffusion energies of Na(0) and Na' on BASE are given in Table 1.

Distances for travel of electrons by tunneling and ions by diffusion, in competition with desorption are calculated from a 1-D random walk model.

DESCRIPTION OF THE MODEL

The most important steps in the reduction of sodium ions in beta'-alumina to neutral sodium atoms are diffusion of sodium ions to the surface of the beta'-alumina and tunneling of electrons to the ion from the porous metal electrode. Na' diffusion in the bulk BASE contributes only to the series ohmic resistance, but also determines which beta'-alumina surface is electro-chemically active. The ion diffusion step in the defect block of bulk beta'-alumina is very fast at surfaces (hk0) with a high density of defect block edges.[12,13] Diffusion through the beta'-alumina spinel block is too slow to allow basal plane surfaces of beta'-alumina, which lack defect block edges, to contribute to the electrochemical reaction.

The model addresses the exchange current at the electrochemically active crystallite faces containing defect block edges. The very high ion diffusion rate in the defect plane and very low ion
diffusion rate through the spinel block are included via the fraction of the ceramic surface which is electrochemically active. This active area is combined with the length of the three phase interface per unit area into a morphology factor for the electrode and solid electrolyte interface. These quantities were measured by scanning electron microscopy and surface decoration experiments.[3]

The last step in the ion diffusion process, from the bulk into a surface site might still limit exchange currents slightly. However, in studies of Na(l)/BASE/Na(l) cells, only an ohmic resistance due to ionic transport is observed above about 673K-723K.[14] The experimental determination and model fitting of the exchange current at porous metal electrodes in AMTEC cells shows that the electrochemical impedance is very small at high sodium gas activities.[2,3]

The tunneling step is very rapid for sodium ions within a primary reaction zone about 1.0 nm from the three phase boundary, but rapidly becomes very slow at greater distances. Following a stretch of an adsorbed sodium ion away from the surface, an electron from the electrode can tunnel to it, forming a sodium atom near its equilibrium position, with high probability.

The spatial extent of the reaction beyond the defect block edge within about 1.0 nm of the Mo electrode may be increased primarily through two mechanisms. The first is hopping of electrons between sodium atoms and sodium ions on the BASE surface with a probability controlled by the distance and the rate of rearrangement by stretching the sodium ion bonding distance to the surface. The second process is diffusion of sodium ions onto the beta"-alumina spinel block surfaces. The first mechanism is very important at lower temperatures where the rearrangement competes very favorably with the higher energy desorption of sodium atoms from the beta"-alumina surface. The second mechanism involves ion transport on the surface and is probably unimportant except at higher temperatures since bond breaking and reformation must occur.

The highest energy activated process necessary to the electrochemical exchange rate is sodium atom desorption from the BASE surface. Therefore, the model must include processes which tend to increase the BASE surface area from which desorption of sodium atoms formed by electron transfer from the electrode can occur. The extent of this area expansion is determined by the relative rates of the activated processes.

Electrons can hop from adsorbed sodium atoms produced in the primary zone, to activated sodium ions further away along the defect block surface to generate a secondary zone from which sodium atoms can desorb.

The tertiary zone is the spinel block surface near the defect block. Sodium ions from the defect block and electrons can diffuse onto this surface, recombine, leading to sodium atom desorption. For the electrochemical exchange reaction area to increase onto the spinel block surface requires that both electrons originally from the electrode and sodium ions originally from the BASE migrate onto this surface and then desorb. Recombination and escape of sodium atoms limits the distances electrons can hop along the defect block and sodium atoms can diffuse. Na⁺ hopping onto and across the spinel block does not compete directly with desorption because the sodium ion desorption energy is large. It competes instead with electron hopping from Na(0) to Na⁺ across the spinel block, a process which is essentially similar to the electron hopping along the defect block. At 600-1000K Na⁺ ions diffuse relatively slowly, but at 1000-1300K they diffuse only a little more slowly than the electrons.

Sodium atoms may also diffuse on this surface prior to desorption. Sodium atom diffusion on the spinel surface of BASE is almost certainly more rapid than the atom desorption rate. Sodium atom diffusion is also likely to be a lower energy process than ion diffusion, because the atom binding energy is less. We expect it to be more important at lower temperatures and to compete less effectively at higher temperatures. Estimating the atom diffusion rate is, but it is probably a too low energy process to contribute
Table 1: Energies important to calculation of exchange current.

<table>
<thead>
<tr>
<th>Process</th>
<th>Approx. Energy (eV)</th>
<th>Approx. Energy (J/atom)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺ diffusion (bulk BASE)</td>
<td>0.16404</td>
<td>2.63x10⁻²⁰</td>
<td>13,14</td>
</tr>
<tr>
<td>Na⁺ diffusion (to surface)</td>
<td>&gt; 0.164 &lt; 0.306</td>
<td>2.63x10⁻²⁰ 4.90x10⁻²⁰</td>
<td>est.</td>
</tr>
<tr>
<td>Na⁺ BASE (surface) binding on spinel block surface defect block surface</td>
<td>1.68 2.18</td>
<td>2.69x10⁻¹⁹ 3.49x10⁻¹⁹</td>
<td>Knotek</td>
</tr>
<tr>
<td>Na⁺O₃ reorganization</td>
<td>0.306 - 0.773</td>
<td>4.905x10⁻²⁰ - 1.238x10⁻¹⁹</td>
<td>calc.</td>
</tr>
<tr>
<td>Na⁺ hop (surface diffusion)</td>
<td>0.685</td>
<td>1.10x10⁻¹⁹</td>
<td>fit</td>
</tr>
<tr>
<td>Na(0) desorption</td>
<td>1.0147</td>
<td>1.63x10⁻¹⁹</td>
<td>CRC</td>
</tr>
<tr>
<td>Na(0) hop (surface diffusion)</td>
<td>&lt; 0.4</td>
<td>6.40x10⁻²⁰</td>
<td>est.</td>
</tr>
</tbody>
</table>

to the discrepancy between the model and experimental data from 1000K to 1300K. Because the Na(0) population on the surface is substantially lower than the Na⁺ population, we expect Na(0) diffusion only to increase the effective reaction area slightly at the lower temperatures and be unimportant at the higher temperatures. Better experimental data and model parameters would be required to assess the contribution of Na(0) diffusion to the exchange current.

The entire electrolyte surface is exposed to collisions with sodium atoms in the gas. As a result there should not be steep concentration gradients of adsorbed alkali atoms and ions when small dc currents flow in the cell. However the chemical exchange process cannot produce perturbations in the ion and atom surface coverage which are correlated to electrode potential. Na(0) adsorption on the spinel block from the gas phase, followed by electron tunneling to the defect block can populate the spinel block with Na⁺ ions, but this process contributes only to the chemical exchange rate.

Both the extension of the reaction zone along the defect block from the primary reaction zone, and onto the spinel block surface can be evaluated as 1-D random walk problems, where the number of steps is determined by competition between activated processes. We take the average extent of the reaction zone to be limited to region where the sodium atom desorption rate is equal to at least half the rate in the primary reaction zone. Electron hopping along the defect block is controlled by competition between the sodium
ion reorganization energy necessary for tunneling, and the sodium atom desorption energy. Both of these processes have been quantitatively evaluated. The spread of sodium ions and electrons onto the spinel block surface are both necessary for sodium atom formation and desorption. The expansion of the reaction zone onto the spinel block surface is controlled by the average extent of migration of the sodium ions before they capture electrons, provided that the electrons do not hop more times than they would on average before sodium atom desorption. The random walk calculation is carried out for a regular sequence of sodium ions each separated by two sites about 0.35 nm from their neighbors.

The calculation of the primary exchange process within about 1.1 nm of the Mo electrode is indicated by the circles in Figure 2. The diamonds include the additional area due to electron hopping on the defect block. The squares also include the reaction area due to sodium ion and electron diffusion onto the spinel block surface. The solid circles are averages of experimentally measured exchange currents. The solid line is a fit to a semi-empirical model based on the collision desorption rate alone and the dotted line is a completely empirical fit to the experimental data.

CONCLUSIONS

This model was built from an attempt to understand the significance of the experimental exchange current. All parameters except the activation energy for sodium ion diffusion were taken from experimental measurements or chemically reasonable calculations. 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, but it begins to put AMTEC electrode mechanistic phenomena at a molecular level on a more quantitative basis.

The absolute agreement of the calculation with experiment is better than expected, given the uncertainty in the morphological parameters especially. The agreement of the temperature dependence of the exchange current was unsatisfactory after the extension of the reaction zone onto the defect block was included, and this drove the fit to the step for diffusion of Na⁺ and e⁻ onto the spinel block surface. That addition involved using the discrepancy to help determine the ion diffusion activation energy, and it is possible that this fit corrects for errors in other parameters in the model. However, the energies used are either measured, or quite reasonable, and the processes include all physically realistic steps consistent with the experimental observation. The agreement indicates that the last step in Na⁺ ion diffusion from bulk to surface is not more greatly activated than the lowest reorganization energy of the Na⁺ on the defect block surface. The agreement at lower temperatures suggests that sodium atom diffusion on the BASE surface has only a small effect on the exchange rate, but cannot be estimated from the experimental data because its activation energy is similar to other more important processes such as Na⁺ diffusion and reorganization.

![Figure 2: Modeled exchange current in 1° zone (circles), plus 2° zone (squares), and 3° (diamonds). The solid line is a semi-empirical fit, filled circles are averaged measured exchange currents.](image)
ACKNOWLEDGEMENTS

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REFERENCES

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