Slow, Steady-State Transport with “Loading” and Bulk Reactions: the Mixed Ionic Conductor La$_2$CuO$_{4+\delta}$

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(Dated: March 22, 2022)

We consider slow, steady transport for the normal state of the superconductor La$_2$CuO$_{4+\delta}$ in a one-dimensional geometry, with surface fluxes sufficiently general to permit oxygen to be driven into the sample (“loaded”) either by electrochemical means or by high oxygen partial pressure. We include the bulk reaction O$\rightarrow$O$^{2-}+2h$, where neutral atoms (a) go into ions (i) and holes (h). This system is a mixed ionic electronic conductor (MIEC). For slow, steady transport, the transport equations simplify because the bulk reaction rate density $r$ and the bulk loading rates $\partial n_0$ then are uniform in space and time. All three fluxes $j$ must be specified at each surface, which for a uniform current density $J$ corresponds to five independent fluxes. These fluxes generate two types of static modes at each surface and a bulk response with a voltage profile that varies quadratically in space, characterized by $J$ and the total oxygen flux $j_0$ (neutral plus ion) at each surface. One type of surface mode is associated with electrical screening; the other type is associated both with diffusion and drift, and with chemical reaction (the diffusion-reaction mode). The diffusion-reaction mode is accompanied by changes in the chemical potentials $\mu$, and by reactions and fluxes, but it neither carries current ($J=0$) nor loads the system chemically ($\partial n_0=0$). Generation of the diffusion-reaction mode may explain the phenomenon of “turbulence in the voltage” often observed near the electrodes of MIEC’s. Within the bulk, the local fluxes satisfy a relation that is independent of the applied fluxes. As a consequence, the bulk response alone cannot match arbitrary values for the five independent input fluxes; matching occurs by generating appropriate amounts of the diffusion-reaction mode at each surface. The bulk response is completely responsible for steady-state loading and typically possesses a voltage profile that varies quadratically in space, as for the lead-acid cell. Seven macroscopic parameters (three $\partial \mu/\partial n$’s, three diffusion constants, and a reaction rate constant) characterize the theory.

PACS numbers: 74.72.-h, 82.33.Pt, 82.45.Xy

I. INTRODUCTION

Mixed ionic electronic conductors (MIECs) are often “loaded” with a specific atom, in either neutral or ionic form. In La$_2$CuO$_{4+\delta}$, atomic or ionic oxygen is loaded into a sample in order to produce a concentration that is more favorable to superconductivity. An idealization of such an experiment would consider a rod of the material in a one-dimensional geometry where fluxes of neutral atoms $a$ ($O$), ions $i$ ($O^{2-}$), and holes $h$ slowly and steadily enter or leave each end (at $x=0$ and $x=L$). Thus, in addition to the material parameters of the system (three thermodynamic, three transport, and one reaction), steady state transport requires specification of six fluxes, subject to the condition that the same net current density $J$ enters and leaves, making a total of five independent fluxes at the two surfaces. Hence, although the rod’s net oxygen content (neutral plus ion) increases with time, its net electric charge remains constant. Once the neutrals or ions enter the rod, they may recombine via the reaction $O \rightarrow O^{2-}+2h$.

A. Chemical Loading and Chemical Reactions

Slow steady transport with loading but without chemical reactions has already been studied for the multiple charge-carrier systems of lead-acid cells and La$_2$CuO$_{4+\delta}$. Because the diffusivities of the charge-carriers differ, the voltage profile within the bulk has a component that varies quadratically in space, the details depending on the fluxes at the surface. These systems support surface modes of only one type, which correspond to electrical screening.

Within the context of semiconductors, slow steady transport with chemical reactions (electron-hole recombination) but without loading has also been studied. Because of recombination (a form of chemical reaction) there is an additional surface mode, but no quadratic variation in space of the voltage profile. The additional mode is associated with diffusion and drift, as well as with recombination, and varies exponentially in space. Although its amplitude is dependent on these fluxes, its structure is independent of the fluxes at the surface.

The present work considers slow steady transport with both loading and chemical reactions. The example again is La$_2$CuO$_{4+\delta}$, since whatever the excess oxygen content $\delta$, there is a way to force oxygen to enter such that reactions must take place to cause equilibration. For example, if all the oxygen enters the bulk as ions (which can be detected
by the conductivity of the sample, then by employing a high pressure atmosphere of molecular oxygen one can expect atomic oxygen to enter the sample, and then convert by reaction to ionic oxygen. Typically, when oxygen is added the fraction that goes into atomic bulk states is neither zero nor unity, so that bulk reactions are needed to cause bulk equilibration. Therefore, we consider an experiment where the surface fluxes of atomic and ionic oxygen are completely arbitrary.

In practice, the specific values of the surface fluxes may or may not be known in a given experiment. Assuming that they are known, in this work we show how one may obtain the response of the MIEC, thus giving the rate of loading of $O$ and $O^{2-}$, the potential, the densities, and the fluxes throughout the sample. Our analysis is valid in the limit of low fluxes, where the equations can be linearized, and for slow steady fluxes. In principle, the fluxes can vary slowly in time. (Slow is loosely defined relative to time it takes for the component with the smallest diffusivity to diffuse across the sample.) Corresponding to the six fluxes specified at the boundaries there must be: at a given surface, a combination of fluxes that specify the amplitude of the exponentially-varying diffusion-reaction mode at that surface; for the bulk, four independent flux combinations that specify the bulk response, which gives a uniform chemical loading within the sample and a uniform current flow through the sample. To our knowledge, this is the first work on any system to consider diffusion and drift, bulk reactions, and surface fluxes general enough to include chemical loading.

B. “Turbulence” at the Interface

Voltage measurement in the area of MIECS is not trivial. The review by Kudo and Fueki notes that “In actual measurements, however, there is often turbulence of the potential distribution in the vicinity of the electrodes with which the electric field is applied.” The authors do not define “turbulence” in any operational sense; it may refer to a complex variation in space or in time. It has become conventional for experiments in this area to place the reference electrodes away from the contact between the MIEC and the adjacent conductors (electronic or ionic), presumably to avoid such “turbulence.” See Figure 1.

If turbulence refers only to a complex variation in space, then it could be due to surface modes generated near the interface. There are at least two such modes in systems of this sort: the usual Debye-like screening mode and the above-described diffusion-reaction mode (in more complex systems, there can be multiple diffusion-reaction modes). The reference electrodes measure “voltages” $\phi_{\text{ref}}$ proportional to electrochemical potentials $\mu$ ($\phi_h = \mu_h/e$ for hole conduction, and $\phi_i = -\mu_i/2e$ for divalent anion conduction). Corresponding to the “voltages” are the “fields” $E_{h,i} = -\partial_x \phi_{h,i}$. Since the screening mode involves no change in the electrochemical potentials, the reference electrodes do not respond to the screening mode. On the other hand, the electrodes do respond to the diffusion-reaction mode.

C. Outline of Paper

Sect.II employs the methods of irreversible thermodynamics, including the effects of chemical reactions, to obtain the transport equations for mixed ionics, including the effects of reactions. Sect.III obtains the steady-state surface modes. Sect.IV obtains the steady-state bulk response. Sect.V discusses how to extract the parameters of the system from measured quantities. Sect.VI presents our conclusions.
II. IRREVERSIBLE THERMODYNAMICS

Consider, in one-dimension, a uniform sample of La$_2$CuO$_{4+\delta}$, as in Fig.1. We take the carriers to be holes and ions (O$^{2-}$) produced by neutral oxygen atoms O via the reaction

$$O \to O^{2-} + 2h$$  \hfill (1)

with reaction rate density $r$.

A. General Considerations

Let $u$ denote the energy density, $T$ the temperature, $s$ the entropy density, $\tilde{\mu}_h$, $\tilde{\mu}_i$, and $\tilde{\mu}_a$ the hole $h$, ion $i$, and neutral atom $a$ electrochemical potentials, and $n_h$, $n_i$, and $n_a$ the corresponding number densities. Then the fundamental thermodynamic differential for this system is

$$du = Tds + \tilde{\mu}_h dn_h + \tilde{\mu}_i dn_i + \tilde{\mu}_a dn_a.$$  \hfill (2)

With $\mu_h$, $\mu_i$, and $\mu_a$ the chemical potentials, and $\phi$ the electrical potential, we have

$$\tilde{\mu}_h \equiv \mu_h + e\phi, \quad \tilde{\mu}_i \equiv \mu_i - 2e\phi, \quad \tilde{\mu}_a \equiv \mu_a.$$  \hfill (3)

Here $\phi$ satisfies Poisson’s equation

$$\nabla^2 \phi = -\frac{\rho}{\varepsilon} = -\frac{e}{\varepsilon}(-2n_i + n_h),$$  \hfill (4)

where $\varepsilon$ is the dielectric constant, a multiple of the permittivity of free space $\varepsilon_0$, and the charge density

$$\rho = e(-2n_i + n_h).$$  \hfill (5)

The conservation laws for this system are, in one-dimension ($x$)

$$\partial_t u + \partial_x j^u = 0, \quad \partial_t s + \partial_x j^s = \frac{\mathcal{P}}{T} \geq 0,$$  \hfill (6)

$$\partial_t n_h + \partial_x j^h = 2r, \quad \partial_t n_i + \partial_x j^i = r, \quad \partial_t n_a + \partial_x j^a = -r.$$  \hfill (7)

Here $j^u$ is the energy flux density, $j^s$ is the entropy flux density, $\mathcal{P}$ is the rate density of heat production ($\mathcal{P}/T$ is rate density of entropy production), $j^h$ is the hole number flux density, $j^i$ is the ion number flux density, and $j^a$ is the neutral atom number flux density. In Fig.1, the signs of $r$ are taken such that if $O \to O^{2-} + 2h$, then $n_h/2$ and $n_i$ increase at the same rate that $n_a$ decreases. The fluxes, $r$, and $\mathcal{P}$ are to be determined.

The time-derivatives of (3) and (7) lead to

$$0 \leq \mathcal{P} = -\partial_t j^u + T \partial_x j^s - \tilde{\mu}_h(2r-\partial_x j^h) - \tilde{\mu}_i(r-\partial_x j^i) - \tilde{\mu}_a(-r - \partial_x j^a)$$

$$= -\partial_x (j^u - Tj^s - \tilde{\mu}_h j^h - \tilde{\mu}_i j^i - \tilde{\mu}_a j^a)$$

$$- j^s \partial_x T - j^h \partial_x \tilde{\mu}_h - j^i \partial_x \tilde{\mu}_i - j^a \partial_x \tilde{\mu}_a - r(2\tilde{\mu}_h + \tilde{\mu}_i - \tilde{\mu}_a).$$  \hfill (8)

Expressing $\mathcal{P}$ as a non-negative quadratic form uniquely requires that: (a)

$$j^u = Tj^s + \tilde{\mu}_h j^h + \tilde{\mu}_i j^i + \tilde{\mu}_a j^a;$$  \hfill (9)

that (b)

$$j^s = -\frac{K}{T} \partial_x T - \alpha^{sh} \partial_x \tilde{\mu}_h - \alpha^{si} \partial_x \tilde{\mu}_i - \alpha^{sa} \partial_x \tilde{\mu}_a,$$  \hfill (10)

where $\kappa \geq 0$ is the thermal conductivity; that (c)

$$j^h = -\alpha_{hh} \partial_x \tilde{\mu}_h - \alpha_{hi} \partial_x \tilde{\mu}_i - \alpha_{ha} \partial_x \tilde{\mu}_a - \alpha_{ha} \partial_x T,$$

$$j^i = -\alpha_{ih} \partial_x \tilde{\mu}_h - \alpha_{ii} \partial_x \tilde{\mu}_i - \alpha_{ia} \partial_x \tilde{\mu}_a - \alpha_{ia} \partial_x T,$$

$$j^a = -\alpha_{ah} \partial_x \tilde{\mu}_h - \alpha_{ai} \partial_x \tilde{\mu}_i - \alpha_{aa} \partial_x \tilde{\mu}_a - \alpha_{aa} \partial_x T,$$  \hfill (11)
where \( \alpha_{hh} \geq 0, \alpha_{ii} \geq 0, \) and \( \alpha_{aa} \geq 0, (\kappa/T)\alpha_{hh} \geq \alpha_{aa}^2, (\kappa/T)\alpha_{ii} \geq \alpha_{aa}^2, (\kappa/T)\alpha_{aa} \geq \alpha_{aa}^2, \) and \( \alpha_{hh}\alpha_{ii} \geq \alpha_{aa}^2, \) etc. (by the Onsager symmetry principle). \( \alpha_{hi} = \alpha_{ih}, \alpha_{sh} = \alpha_{hs}, \) and \( \alpha_{si} = \alpha_{is} \); and that (d)

\[
r = -\lambda(2\bar{\mu}_h + \bar{\mu}_i - \mu_a) = -\lambda(2\bar{\mu}_h + \bar{\mu}_i - \mu_a).
\]

where the reaction parameter \( \lambda \geq 0 \) is related to the hole and ion lifetimes \( \tau_h \) and \( \tau_i \). In equilibrium \( r = 0 \), so (12) implies that the change in Gibbs free energy be zero, or \( 0 = 2\bar{\mu}_h^{(0)} + \bar{\mu}_i^{(0)} - \mu_a^{(0)} \), as expected. For slow steady processes, \( r \) need not be zero but, as we will see, \( r \) will take a value consistent with the surface fluxes, and \( r \) will be uniform in space and in time.

### B. Specific Considerations

From here on, we neglect any coupling to entropy or temperature, and any off-diagonal coupling. Thus \( 0 = \alpha_{is} = \alpha_{ha} = \alpha_{si} = \alpha_{ia} \). Moreover, we employ \( \alpha_{h} \equiv \alpha_{hh}, \alpha_{a} \equiv \alpha_{aa}, \) and \( \alpha_{i} \equiv \alpha_{ii} \).

We write the densities in the form

\[
n = n^0 + \Delta n, \tag{13}
\]

where \( n^0 \) is the equilibrium value and \( \Delta n \) is the deviation from equilibrium (\( \delta n \) will be reserved for terms that vary in space, either in the surface solution or in part of the bulk response). We now linearize \( r \) as

\[
r = -\lambda(2\bar{\mu}_h + \bar{\mu}_i - \mu_a) = -\lambda(2\bar{\mu}_h + \bar{\mu}_i + \Delta n_i - \mu_a \Delta n_a). \tag{14}
\]

Defining the reaction rates \( w \) (with dimensions of inverse time) as

\[
w_h = \lambda \frac{\partial \mu_h}{\partial n_h}, \quad w_i = \lambda \frac{\partial \mu_i}{\partial n_i}, \quad w_a = \lambda \frac{\partial \mu_a}{\partial n_a}, \tag{15}
\]

becomes

\[
r = -(2w_h \Delta n_h + w_i \Delta n_i - w_a \Delta n_a). \tag{16}
\]

Because the \( w \)'s vary as the product of a thermodynamic derivative and the reaction parameter, they can be thought of as “thermo-reaction” parameters.

Linearizing the fluxes and neglecting the off-diagonal terms, (11) becomes

\[
\begin{align*}
\dot{j}^h &= -\alpha_h \partial_x \bar{\mu}_h = -\alpha_h \partial_x (\mu_h + e\phi) = -\alpha_h \left( \frac{\partial \mu_h}{\partial n_h} \partial_x n_h + e \partial_x \phi \right), \tag{17}
\end{align*}
\]

\[
\begin{align*}
\dot{j}^i &= -\alpha_i \partial_x \bar{\mu}_i = -\alpha_i \partial_x (\mu_i - 2e\phi) = -\alpha_i \left( \frac{\partial \mu_i}{\partial n_i} \partial_x n_i - 2e \partial_x \phi \right), \tag{18}
\end{align*}
\]

\[
\begin{align*}
\dot{j}^a &= -\alpha_a \partial_x \bar{\mu}_a = -\alpha_a \partial_x \mu_a = -\alpha_a \left( \frac{\partial \mu_a}{\partial n_a} \partial_x n_a \right). \tag{19}
\end{align*}
\]

The charge-carrier conductivities \( \sigma \) are related to the \( \alpha \)'s via

\[
\sigma_h = e^2 \alpha_h, \quad \sigma_i = 4e^2 \alpha_i. \tag{20}
\]

In terms of the effective electric fields for the charge carriers,

\[
E_h = -\partial_x \phi_h, \quad E_i = -\partial_x \phi_i, \tag{21}
\]

we have

\[
\dot{j}^h = \alpha_h E_h, \quad \dot{j}^i = -2\alpha_i E_i. \tag{22}
\]

The diffusivities \( D \) are given by

\[
\begin{align*}
D_h &= \alpha_h \frac{\partial \mu_h}{\partial n_h}, \quad D_i = \alpha_i \frac{\partial \mu_i}{\partial n_i}, \quad D_a = \alpha_a \frac{\partial \mu_a}{\partial n_a}. \tag{23}
\end{align*}
\]
Because the $D$’s vary as the product of a thermodynamic derivative and a transport parameter, they can be thought of as “thermo-transport” parameters. Note that the ratio of a $w$ to a $D$ depends only upon reaction and transport, the thermodynamic derivatives cancelling. Such ratios occur for the diffusion-reaction surface mode.

For completeness, we observe that the electric current density is given by

$$J = e(j^h - 2j^i),$$

and the net oxygen mass flux is given by

$$j_O = j^i + j^a.$$  \hspace{1cm} \hspace{1cm} \hspace{1cm} (25)

### III. STEADY-STATE SURFACE MODES

For surface modes we will employ the notation $\delta n$ for the deviation of a number density from equilibrium, and $\delta \phi$ for the deviation of the potential from equilibrium. We also assume that there is a local relation between $n$ and $\mu$, so that (3) can be employed to relate $\delta n$ to $\delta \tilde{\mu}$ and $\delta \phi$. Then the linearized form of (4) becomes

$$\nabla^2 \delta \phi = \frac{e}{\varepsilon} (2\delta n_i - \delta n_h) = \frac{e^2}{\varepsilon} \left( \frac{\partial n_h}{\partial \mu_h} + 4 \frac{\partial n_i}{\partial \mu_i} \right) \delta \phi + \frac{e}{\varepsilon} \left( 2 \frac{\partial n_i}{\partial \mu_i} \delta \tilde{\mu}_i - \frac{\partial n_h}{\partial \mu_h} \delta \tilde{\mu}_h \right).$$

\hspace{1cm} \hspace{1cm} \hspace{1cm} (26)

#### A. Screening Surface Mode

A steady-state ($\partial n/\partial t = 0$) solution of the equations occurs for no shift in the electrochemical potentials ($\delta \tilde{\mu} = 0$). In this case local equilibrium holds, so there are no fluxes and the recombination rate $r = 0$. As noted above, this mode cannot be measured by electrodes sensitive to individual electrochemical potentials, although the associated density changes might be susceptible to other types of analysis (optical, chemical, or otherwise). Setting all the electrochemical potentials to zero in (26) then gives

$$\nabla^2 \delta \phi = \frac{e^2}{\varepsilon} \left( \frac{\partial n_h}{\partial \mu_h} + 4 \frac{\partial n_i}{\partial \mu_i} \right) \delta \phi.$$ (27)

This has solution

$$\delta \phi = A \exp(-x/l) + B \exp(x/l), \hspace{1cm} \frac{1}{l^2} = \frac{e^2}{\varepsilon} \left( \frac{\partial n_h}{\partial \mu_h} + 4 \frac{\partial n_i}{\partial \mu_i} \right).$$ (28)

This screening mode has screening, or Debye, length $l$ given by (28). This mode depends only upon equilibrium properties of the system. Note that the neutral atoms do not participate at all.

#### B. Diffusion and Reaction Surface Mode

Another steady-state ($\partial n/\partial t = 0$) solution is obtained by considering the case where $r \neq 0$. Comparison of the three terms in the continuity equations (7) gives the conditions

$$j^h/2 = j^i = -j^a.$$ (29)

Note that (29) implies $J = 0$ (no current flow) and $j_O = j^i + j^a = 0$ (no net oxygen flow). By the flux equations (11), the variations in electrochemical potential then satisfy

$$-\alpha_h \delta \tilde{\mu}_h/2 = -\alpha_i \delta \tilde{\mu}_i = \alpha_a \delta \tilde{\mu}_a.$$ (30)

Thus (12) can be rewritten as

$$r \approx -2 \lambda \alpha_h \delta \tilde{\mu}_h \left( \frac{1}{\alpha_h} + \frac{1}{4 \alpha_i} + \frac{1}{4 \alpha_a} \right).$$ (31)

Using this in the steady-state version of (17) for $j^h$ then gives

$$-\alpha_h \partial_x^2 \tilde{\mu}_h = -4 \lambda \alpha_h \delta \tilde{\mu}_h \left( \frac{1}{\alpha_h} + \frac{1}{4 \alpha_i} + \frac{1}{4 \alpha_a} \right).$$ (32)
This diffusion-reaction mode has diffusion-reaction length $L$ given by (33). All three mobile species contribute to this mode. Since the $\alpha$’s are related to diffusion, this mode depends both upon diffusion ($\alpha$) and reaction ($\lambda$). The faster the diffusion (i.e. the larger the $\alpha$), the larger the $L$; the faster the reaction (i.e. the larger the $\lambda$), the shorter the $L$. This qualitative dependence on diffusion and reaction is as expected. A similar mode occurs for semiconductors, where the chemical reaction involves the recombination of electrons and holes.

If any of these mobile species has a very slow rate of transport, corresponding to a small $\alpha$, then $L$ is very short. As a consequence, within a short distance of the surface the system can adjust from surface-determined boundary conditions to the bulk values.

For this mode, if $\delta \bar{\mu}_h = (C/\alpha_h) \exp(-x/L)$, then by (30)

$\delta \bar{\mu}_h = \frac{C}{\alpha_h} \exp(-x/L), \quad \delta \bar{\mu}_i = \frac{C}{2\alpha_i} \exp(-x/L), \quad \delta \mu_a = -\frac{C}{2\alpha_a} \exp(-x/L). \quad (34)$

By (30) the potential $\delta \phi$ is given by

$$(\frac{1}{L^2} - \frac{1}{L^2}) \delta \phi = -\frac{e}{\varepsilon} \left( \frac{\partial n_i}{\partial \mu_i} \frac{1}{\alpha_i} - \frac{\partial n_h}{\partial \mu_h} \frac{1}{\alpha_h} \right) C \exp(-x/L). \quad (35)$$

This equation relates $A$ of (33) to $C$ of (34).

Since the potential $\delta \phi$ of (33) is non-zero for the diffusion-reaction mode, this mode also involves the electric field.

Finally, note that associated with any steady-state surface mode, where $\partial n = 0$, there is no deposition of material near the surface. For the present model, where there are both fluxes and chemical reactions, whatever component is produced by chemical reactions ($r \neq 0$) is taken up by nonuniform flux ($\partial x, j \neq 0$).

If $j_O = j^i + j^a$ is non-zero for the bulk response, the diffusion-reaction mode (with $j_O$ non-zero but $j^i$ and $j^a$ individually non-zero) has the important property that, when added to the bulk mode, it can change the flux ratio $j^i/(j^i + j^a)$ on moving from the surface to a few $L$ within the bulk.

IV. STEADY BULK TRANSPORT RESPONSE

There are two types of bulk transport response, according to whether or not the system is being chemically loaded.

A. Steady Bulk Transport Response – No Chemical Loading

One solution of the steady-state equations (where $\partial x n_h = 0$, etc.) occurs for $\delta n_h = \delta n_i = \delta n_a = 0$, but $\delta \phi = -Ex + D$, corresponding to a uniform shift in the electrical potential and a uniform field $E_x = E$. This leads to constant partial currents $j^h = \alpha_h E$, $j^i = -2\alpha_i E$, $j^a = 0$, and corresponds to no chemical loading, although there is a net oxygen flux that crosses the system. The solution we obtain in the next section is sufficiently general that it includes this case, which will serve as a check on the results of the next section.

B. Steady-state Bulk Flow with Chemical Loading, so $\partial x n \neq 0$

Consider a situation with two electrode surfaces, one at $x = 0$ and the other at $x = L$. Let there be slow steady flow, and at the surfaces let the ion, atom, and hole fluxes $j^i$, $j^a$ and $j^h$ be specified, subject to equal net electric current densities $J$ at the surfaces (so there is no electrical charging). However, there can be unequal net oxygen fluxes $j^i + j^a$ at the surfaces, so a net amount of oxygen can be loaded into the system (mass charging). Thus, we specify the fluxes at the boundaries, and within the system we must determine the potential, the fluxes, and the densities. This leads to five input fluxes, which may be thought of as $J$, the two net oxygen fluxes $j^i + j^a$ at each surface, and the flux ratios $j^i/(j^i + j^a)$.

As a guide to solving the present problem, note that Ref. considered, in one dimension, slow steady discharge of a lead-acid cell for concentrations where reactions were unimportant. (Two and three dimensions have also been considered.) It was found that the mass loading (and for discharge, unloading), given by $\partial x n$ (for ions $H^+$ and
HSO$_4^-$, is uniform in space and time, so the background densities decreased uniformly in space and time. The continuity equation then implied that the fluxes vary linearly in space and are constant in time. It was then found that all of the vector quantities in this problem – two fluxes, two density gradients, and the electric field – vary linearly in space and are constant in time. The two ion densities have the same gradients, but they have a constant offset, leading to a constant non-zero charge density that is proportional to the current flow. This does not violate charge conservation because the screening modes at the surfaces can take up the excess charge.

In the present case we assume that the bulk response has a reaction rate density $r$ and the $t$ is uniform both in space and in time. As a consequence of (38), the charge density $\rho$ also is uniform in space ($\partial_x \rho = 0$) and in time ($\partial_t \rho = 0$). For fixed $J$ and $j^i + j^h$ at each surface, but unspecified flux ratios $j^i/j^i + j^h$, this leads to a consistent solution of the equations for this system; since the equations are linear, the solution is unique. The uniformity assumption leads to a local constraint on the fluxes, and thus specifies the flux ratios at the surfaces. By adding in appropriate amounts of the diffusion-reaction mode at each surface, the flux ratio of the total system can be made to correspond to any experimental values for the net flux ratios.

1. General Considerations

The charge continuity equation is given by

$$\partial_t \rho + \partial_x J = 0. \quad (36)$$

The assumption that $\partial_t \rho = 0$ implies that $J$ is constant in space and in time, consistent with our taking $J$ to have the same value at each surface. Moreover, $\partial_t \rho = 0$ implies there is no electrical charging, so the electric charge and the field $E$ and potential $\phi$ that it produces should all be constant in time. The assumption that $\partial_x \rho = 0$ implies, if $\rho$ is non-zero, that the field varies linearly in space, and that the potential varies quadratically in space, results that we will show are consistent with the other equations. These properties are shared by the slowly discharging lead-acid cell and chemically loaded La$_2$CuO$_{4+\delta}$ without reactions.

Adding the second two equations of (7) yields what amounts to conservation of the sum of $O^{2-}$ ions and $O$ atoms:

$$\partial_t (n_i + n_a) + \partial_x (j^i + j^a) = 0. \quad (37)$$

By (37), since the $\partial_t n$’s are assumed to be constant in space and time, the net oxygen flux $j_O = j^i + j^a$ varies linearly in space, and can be determined in the bulk from its values at the two ends of the sample.

From the continuity equations (7), the constancy in space and time of $r$ and the $\partial_t n$’s then implies that the slopes of all the fluxes are independent of space and time. Hence, in the absence of surface modes, these fluxes $j^n$, $j^i$ and $j^h$ are given by a linear interpolation between their values at the boundaries. We will see that, because the fluxes vary linearly in space, so do the other vector quantities in the problem: $\partial_t n_i$, $\partial_x n_e$, and $E = E_x = -\partial_x \phi$. (We have already argued that $E$ is linear in space.)

Let us rewrite Poisson’s equation (4) in terms of $E = -\partial_x \phi$. This gives Gauss’s Law which, in one-dimension, reads

$$\partial_x E = \frac{\rho}{\varepsilon} (-2n_i + n_h). \quad (38)$$

Taking the $x$-derivative of (38), and using the flux equations to eliminate $\partial_x n_i$ and $\partial_x n_h$, gives

$$\partial_x^2 E = \frac{\epsilon}{\varepsilon} (4 \partial_{\mu_i} n_i + \epsilon \partial_{\mu_h} n_h) E + \frac{\epsilon}{\varepsilon} \left( \frac{\partial n_i}{\partial \mu_i} \alpha_i - \frac{\partial n_h}{\partial \mu_h} \alpha_h \right). \quad (39)$$

This is solved by assuming that $E$ is linear in $x$, so $\partial_x^2 E = 0$. Then (39) gives $E$ as a linear combination of the $j$’s. Since the $j$’s vary linearly in $x$, then so does $E$, and our assumption that $E$ is linear in $x$ is consistent. Explicitly, (39) gives

$$E = -\partial_x \phi = -\frac{1}{\epsilon (\partial_{\mu_h} + 4 \partial_{\mu_i})} \left[ \frac{\partial n_h}{\partial \mu_h} \frac{j^h}{\alpha_h} + \frac{2}{\partial \mu_i} \frac{j^i}{\alpha_i} \right]. \quad (40)$$

Since, unless the values of $j^i$ and $j^h$ at the surface conspire to give no linear term in $E$ of (40), $E$ typically will vary linearly in space. Thus the potential $\phi$ typically will vary quadratically in space. Moreover, $\partial_x E$ typically is uniform in space, so by (38) the charge density $\rho = \epsilon (-2n_i + n_h)$ typically is uniform in space, consistent with our assumption that $\partial_x \rho = 0$. 

Application of $\partial_x \rho = 0$ to (5) gives

$$2\partial_x n_i = \partial_x n_h.$$  \hfill (41)

Eqs. (40) and (41), and the relations (19) then give

$$2\partial_x n_i = \partial_x n_h = -\left(\frac{\partial n_h}{\partial n_a} \frac{\partial n_a}{\partial \mu} + 4\frac{\partial n_h}{\partial \mu}\right)\left(2\frac{j^i}{\alpha_i} + 4\frac{j^h}{\alpha_h}\right).$$  \hfill (42)

Since the $j'$s are linear in space, so are these two density gradients.

We have already assumed that $r$ of (16) is independent of $x$, or $0 = \partial_x r$. Using (11) and (16) leads to

$$\partial_x n_a = \frac{4w_h + w_i}{w_a} \partial_x n_i = \frac{4\frac{\partial n_h}{\partial n_a} + \frac{\partial n_i}{\partial \mu}}{\partial n_a} \partial_x n_i,$$  \hfill (43)

so all three density gradients are linear in space.

As a consequence of (43) and (42), (19) yields the condition

$$j^a = -\alpha_a \left(\frac{\partial n_a}{\partial n_a}\right) \partial_x n_a = \frac{\alpha_a}{\alpha_i} j^i + 2\frac{\alpha_a}{\alpha_h} j^h.$$  \hfill (44)

Thus, for the bulk response, $j^a$ has a specific dependence on $j^i$ and $j^h$. If (12) is not satisfied at either boundary, then diffusion-recombination modes are generated, with amplitudes determined in subsection IV.C.

2. Specific Considerations

We can now obtain explicit values for the three fluxes, the field, and the three density gradients.

(a) With a knowledge of the mass flux $j_0 = j^i + j^a$ at each end of the sample, of the current $J = e(-2j^i + j^h)$, and of the condition (14), one can obtain explicit values for all three $j$’s. This gives

$$j^i = j_0 - \frac{2\alpha_a}{\alpha_h} \frac{(J/e)}{1 + \frac{\alpha_a}{\alpha_i} + 4\frac{\alpha_a}{\alpha_h}},$$  \hfill (45)

$$j^h = \frac{2j_0 + \frac{2\alpha_a}{\alpha_i} \frac{(J/e)}{1 + \frac{\alpha_a}{\alpha_i} + 4\frac{\alpha_a}{\alpha_h}}}{1 + \frac{\alpha_a}{\alpha_i} + 4\frac{\alpha_a}{\alpha_h}},$$  \hfill (46)

$$j^a = \frac{(\frac{\alpha_a}{\alpha_i} + 4\frac{\alpha_a}{\alpha_h})j_0 + 2\alpha_a (J/e)}{1 + \frac{\alpha_a}{\alpha_i} + 4\frac{\alpha_a}{\alpha_h}}.$$  \hfill (47)

(b) With a knowledge of the three $j$’s and $E$, by the flux equations (19) we can obtain explicit values for the three density gradients $\partial_x n$. Since the $\partial_x n$’s all are proportional to $j^a$ (as given above), we do not present them here. Like the three $j$’s and $E$, the $\partial_x n$’s vary linearly in space. We measure the associated deviations $\delta n$ from $x = 0$, so that

$$\delta n = \int_0^x \partial_x n \, dx.$$  \hfill (48)

Let us now write each density $n$ as the sum of its equilibrium value $n^{(0)}$ and its deviation $\Delta n$, where the latter consists of three terms: an offset term $\Delta$ that is constant both in space and in time (and has yet to be determined), a term at (where $\partial_t n = a$) that is constant in space but linear in time (this corresponds to chemical loading at a uniform rate, and has yet to be determined; we must also satisfy $at \ll n^{(0)}$), and a spatially-varying term $\delta n$ that is constant in time but has a non-zero spatial variation (that has in principle been determined):

$$n_e = (n^{(0)}_h + \Delta_h) + a_h t + \delta n_h, \quad n_i = (n^{(0)}_i + \Delta_i) + a_i t + \delta n_i, \quad n_a = (n^{(0)}_a + \Delta_a) + a_a t + \delta n_a.$$  \hfill (49)
Note that \( n_0^h = 2n_0^h \), since the system is neutral in equilibrium, and \( n_0^h \) is (in principle) known from the equilibrium thermodynamics.

We can now obtain explicit values for the three \( a \)'s.

(a) Since we assumed that \( \partial_t \rho = 0 \), by (5) we have
\[
2\partial_t n_i = \partial_t n_h.
\]
Eq. (50), when applied to (49) gives
\[
a_h = 2a_i.
\]

(b) The requirement that \( r \) of (16) satisfy \( \partial_t r = 0 \), when combined with (51), leads to
\[
a_a = \frac{4w_h + w_i}{w_a}a_h = \frac{4\partial n_h + \partial n_i}{\partial n_a}a_h.
\]

(c) Since \( j^i \) and \( j^a \) are known by linearly interpolating their values at the boundaries, \( j^i + j^a \) is known. Hence (51) gives
\[
a_h + a_a = -\partial_x (j^i + j^a).
\]

This, with (51) and (52), then determines all three \( a \)'s, thus specifying the time-dependences of the \( n \)'s.

We can now obtain explicit values for the three \( \Delta \)'s, which correspond to deviations from true equilibrium values.

(a) Since \( E \) is known from (40), by (38) so are \( \partial_x E \) and \( \rho = \varepsilon \partial_x E \). Thus, by (5),
\[
n_h - 2n_i = \Delta_i - 2\Delta_h = \frac{\rho}{\varepsilon} = \frac{\varepsilon}{\varepsilon} \partial_x E
\]
is determined, where \( \partial_x E \) is obtained from a version of (40) with the fluxes replaced by their (constant) gradients.

(b) Eq. (7) for \( \partial_t n_h \) can be used to determine \( r \) in terms of \( a_h \) and \( \partial_x j^h \). The three continuity equations have already been used twice, once for charge, and once for oxygen, so that this is their third and final allowable use. From \( r \) we can obtain \( \Delta_a \) by (16), written as
\[
r \approx -(2w_h\Delta_h + w_i\Delta_i - w_a\Delta_a).
\]

(c) The arbitrariness in time-origin for the terms \( at \) in the \( n \)'s permits us to set one of the \( \Delta \)'s to zero, so we may take
\[
\Delta_h = 0.
\]
The relations (51), (52), and (56) determine all three \( \Delta \)'s.

Thus we have obtained the time variation \( at \), the spatial variation \( \delta n \), and the offset \( \Delta \) for each \( n \).

Note that the reaction rate density \( r \), and the \( \partial n/\partial t \)'s are independent of position and of time, as assumed.

The steady-state bulk solution we have obtained is very general, having three free parameters (the current and the net mass fluxes at each surface), but the most general steady-state bulk solution has five free parameters. By adding in a diffusion-reaction mode at each surface, we can maintain the same current and net mass fluxes at each surface, yet still permit five free parameters. Hence, since the equations are linear, in obtaining one steady-state solution, we have obtained the steady-state solution.

The results above hold even if the fluxes are slowly varying in time, provided one uses the instantaneous values of the fluxes. In this case the \( a \)'s also are slowly varying with time, but their dominant dependence on time is given by the above approach.

\section*{C. Using Surface Solutions to Match the Boundary Conditions}

Assuming arbitrary fluxes at the boundaries, we now determine how much of each type of response (bulk and surface) is generated.

First, note that (14) applied to our specific bulk response (to which we append the subscript \( b \)), can be rewritten as
\[
j^a_b = \frac{\alpha_a}{\alpha_i} j^i_b + 2\frac{\alpha_a}{\alpha_h} j^h_b.
\]
Now note that the electric current density of \( \mathbf{J} \),

\[
J = e (j^b_h - 2j^h_b),
\]

(58)
is uniform in space, so it holds both in bulk (b) and at edges (E). With (58), (59) can be rewritten as

\[
j^b_h = \left( \frac{\alpha_a}{\alpha_h} + \frac{\alpha_a}{\alpha_i} \right) j^i_h + 2 \frac{\alpha_a}{\alpha_h} \frac{J}{e}.
\]

(59)

At either edge E, write

\[
j^b_h = j^E_h - \Delta j^a_h, \quad j^i_h = j^E_h + \Delta j^a_h,
\]

(60)

where \( j^E_h \) and \( j^E_i \) are the (in principle known) total O and O\(^{2-}\) fluxes at the edge, and \( \Delta j^a_h = -\Delta j^a_i \) are the amplitudes due to the surface solutions. Substituting both parts of (60) into (59) then yields

\[
(1 + \frac{\alpha_a}{\alpha_h} + 4 \frac{\alpha_a}{\alpha_i}) \Delta j^a_E = j^a_E - (\frac{\alpha_a}{\alpha_h} + \frac{\alpha_a}{\alpha_i}) j^i_E - 2 \frac{\alpha_a}{\alpha_h} \frac{J}{e} = j^a_E - \frac{\alpha_a}{\alpha_i} j^i_E - 2 \frac{\alpha_a}{\alpha_h} j^h_i.
\]

(61)

Hence, from a knowledge of all three fluxes at an edge E, and the ratios \( \alpha_a/\alpha_h \) and \( \alpha_a/\alpha_i \), the associated surface solution amplitude \( \Delta j^a_E \) can be determined. By (24), \( \Delta j^a_E/2 = \Delta j^a_i = -\Delta j^a_h \).

Global electroneutrality may be maintained by adding in screening modes, with the appropriate amplitude, at each surface. The specific value of the screening mode amplitudes will depend upon the nature of the contact at the surface, including the electrical contact resistance. Moreover, there can be a dipole layer at the surface, so the \( \text{La}_2\text{CuO}_4\delta \) itself need not be globally electroneutral, only the \( \text{La}_2\text{CuO}_4\delta \) and a small region at each end of the adjacent materials.

The results of this section are sufficiently general that they include those of Sect.IV.A, where there are no density gradients in the bulk, and uniform flow of ions \( (j^i) \) and holes \( (j^h) \). Note that if the surface values of \( j^i \) equal the bulk values, then no diffusion-reaction modes are generated at the surfaces. If the surface values of \( j^i \) are zero (i.e. high pressure oxygen on one end and low-pressure oxygen on the other end), then the input flux of oxygen must come in the form of atoms with \( j^0 \) non-zero, and the diffusion-reaction modes then permit the system to convert atoms to ions within the diffusion-reaction length of the surface.

V. ON COMPARISON TO EXPERIMENT

Comparison to experiment requires a knowledge of the three thermodynamic derivatives \( \partial \mu/\partial n \), the three diffusivities \( D \) (or the three \( \alpha \)'s), and the reaction constant \( \lambda \), which are independent of the fluxes applied to the system. Inclusion of the five independent fluxes at the surface means that the theory for steady state transport involves twelve independent quantities. The question then is how they may be determined.

In principle, equilibrium measurements can yield the three \( \partial \mu/\partial n \)'s. Measurement of \( l \) for the screening mode can provide an additional constraint on the \( \partial \mu/\partial n \)'s.

The fluxes and fields do not depend upon the reaction parameter \( \lambda \). It appears that \( \lambda \) most easily can be obtained by measuring \( L \) for the diffusion-reaction mode, provided that the \( \partial \mu/\partial n \)'s already are known.

DC current measurements with electrodes that do not permit chemical loading, and AC current measurements with any set of electrodes, give \( \sigma_i + \sigma_h \).

Measuring electrodes for holes and ions yield effective fields

\[
E_h = \frac{j^h}{\alpha_h}, \quad E_i = -\frac{j^i}{2\alpha_i}.
\]

(62)

Thus measurements with either type of blocking electrode (for holes or ions) gives two combinations of coefficients, one for \( j_O = j^i + j^a \) and one for \( J/e \). Because the equations for the effective fields hold for all \( j_O \) and \( J/e \), these coefficients are overdetermined.

VI. CONCLUSIONS

We have developed the theory of slow steady transport for \( \text{La}_2\text{CuO}_4+\delta \), including both loading and chemical reactions. We have employed the principles of irreversible thermodynamics, in which appear the thermodynamic
derivatives $\partial\mu/\partial n$, the diffusion constants $D = \alpha(\partial\mu/\partial n)$, and the reaction constant $\lambda$. There are two surface modes, one associated with screening, and the other associated both with diffusion and drift, and with chemical reactions. The screening mode is an equilibrium response, with no fluxes at all. The diffusion-reaction mode has no current flux or mass flux, but non-zero atom, ion, and hole flux. For a given uniform current density $J$ and mass flux at each surface, the system has a special bulk response where the reaction rate density and the mass loading are uniform in space and in time. By adding in the diffusion-reaction modes at each surface, general steady-state solutions are obtained.

As a consequence of the generality of the boundary conditions considered, the present work applies both to oxygen partial pressure loading and electrochemical loading of $\text{La}_2\text{CuO}_4^{+\delta}$. Moreover, given the complex nature of the bulk solution, it is highly unlikely that the material parameters are such that either oxygen partial pressure loading or electrochemical loading will be able to avoid generating diffusion-reaction modes. By varying the imposed current and mass fluxes at each surface, it should be possible to obtain a number of constraints on the parameters appearing in the theory. Thus it would be of great interest to be able to apply the present results to an actual system. Moreover, the diffusion-reaction may be responsible for the puzzling phenomenon of “turbulence of the voltage” near the electrodes, and measurement of its length $L$ would further constrain the values of the material parameters.

Acknowledgments

I would like to thank Allan Jacobson for many valuable conversations. I also would like to acknowledge the Department of Energy for their support under DOE Grant No. DE-FG03-96ER45598.

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