Recent advancements in liquid metal batteries (LMBs) have demonstrated the feasibility of constructing high-capacity-energy storage devices out of a plurality of liquid alloy combinations of alkali or alkaline-earth metals and metalloids as depicted in Figure 1.1 As a step toward specifying the limits of the LMB performance envelope, herein we investigate one of the relevant kinetic processes that govern the electrical output of the cell—the charge-transfer reaction at the positive electrode.

As the name suggests, the active components of LMB cells are two liquid metal electrodes separated by a molten salt electrolyte. The three mutually immiscible liquids phase-separate into a vertically layered stack, as shown in Figure 1. Electrochemical processes at liquid metal/molten salt interfaces are by their very nature exceedingly fast. The high temperatures translate to high thermal energies and the liquid-liquid interfaces contribute low activation energies.2 These features combine to elevate the standard rate constant of charge transfer, wherein we investigate one of the relevant kinetic processes that govern the electrical output of the cell—the charge-transfer reaction at the positive electrode.

Electrochemical alloying/de-alloying at liquid electrodes has seen limited study at high temperatures. Castrilloje et al. have explored electrochemical alloying of rare-earth metals at liquid electrodes,4,5 which exhibit low solubility limits and relatively slow charge transfer kinetics ($k_0 \sim 10^{-3}$ cm/s). Kisz et al. investigated the reaction of sodium at a lead electrode utilizing a combination of chronopotentiometric relaxation and modified electrochemical impedance spectroscopy and reported an exchange current density exceeding 100 A/cm$^2$ ($k_0 > 0.1$ cm/s). Due to the huge disparity in these $k_0$ values, both measured under alloying conditions, it was deemed prudent to explore electrochemical alloying at liquid alloy electrodes of interest to LMB cells.

Various liquid metal battery chemistries have been tested to date, including Na-Bi,6 Mg-Sb,7 Ca(Mg)-Bi,8 Ca-Sb,9 Li-Pb-Sb,10 and Li-Bi.11 For the purpose of this study, the Mg-Sb and Li-Bi couples were chosen for two main reasons: (1) relative stability with their respective molten salt electrolytes and (2) itinerant ions of different valence: Li$^+$ vs. Mg$^{2+}$. The charge transfer kinetics of each couple were studied as a function of alloy concentration by the galvanostatic pulse method in a three-electrode cell with a stable two-phase reference electrode.

**Experimental**

**Electrochemical cell.—** A schematic of the electrochemical cell used for the galvanostatic pulse measurements is shown in Figure 1.
2. Current flows between the working (WE) and counter (CE) electrodes while the potential at the WE is measured with respect to the reference electrode (RE). Not pictured: second RE, tungsten wire inert electrode, and ASTM type-K thermocouple.

**Test vessel.**—Electrochemical measurements were carried out in a stainless steel vessel (pictured in Ref. 14) sealed against the external atmosphere. Seven ports were sealed with O-ring compression fittings, and stainless steel baffle plates provided thermal insulation. The induction-melted electrodes were placed in an alumina crucible with the pre-melted salt. Alumina tubes sealed with epoxy electrically insulated the inert tungsten electrode leads from the test vessel. Assembly was performed in the glove box.

**Electrochemical measurements.**—The drying procedure used for the salt (Materials preparation section) was again performed before bringing the cell to temperature. The two REs equilibrated in less than 2 h, indicating cell stability.

Cyclic voltammetry.—Potential sweeps were performed on the inert (tungsten) electrode to confirm the electrochemical window of the molten salt electrolyte over the potential range of alloying for the Li-Bi and Mg-Sb systems. In addition, potential sweeps at the alloying electrodes were conducted to determine an appropriate cleaning potential.

**Coulometric titration.**—Coulometric titration was used to change the alloy concentration of the WE. First the electrode was cleaned at a potential high enough to remove the alloying species without oxidizing the solvent liquid metal. A cathodic current ($i = -14 \text{ mA}$) was then passed to deposit the desired amount of lithium or magnesium. A rest period of 5,000 s followed to allow for homogenization of the electrode, indicated by a stable open circuit potential (OCP).

The resulting concentration of the liquid alloying electrode, $x_A$, is given by

$$x_A = \frac{n_A}{n_A + n_B} = \frac{-It/zF}{-It/zF + n_B},$$

where $n_i$ is the number of moles of species $i$ in the electrode, $I$ the current, and $t$ the current duration. 100% coulombic efficiency is assumed.

**Galvanostatic transients.**—To determine the exchange current density of alloying/de-alloying at liquid alloy electrodes of various compositions, galvanostatic pulse measurements were performed after coulometric titration. 13 For the charge transfer reaction

$$O + ze^- \leftrightarrow R,$$

where in this work the oxidized species $O$ is $A^{2+}$ and the reduced species $R$ is $A(B)$, the overpotential transient $\eta$ after application of a current pulse $j_0$ is

$$\eta = \frac{RT}{zF} \ln \left( \frac{1}{j_0} + \frac{2}{\pi^{1/2}} N t^{1/2} \right),$$

with

$$N = \frac{1}{zF} \left( \frac{1}{c_{i0}^* D_i^{1/2}} + \frac{1}{c_{i0} D_i^{1/2}} \right),$$

where $D_i$ is the diffusion coefficient of species $i$, and $c_{i0}^*$ the bulk concentration of species $i$. When using the bulk concentrations, $j_0$ is the apparent exchange current density. To be precise, the exchange current density is defined in terms of the instant concentration of...
species \( i \) at the electrode-electrolyte interface, not in terms of its bulk concentration. The first term in the brackets of Equation 5 is the contribution of the charge-transfer reaction to the overpotential \( \eta_{Ct} \), and the second term is the time-dependent mass-transport contribution \( \eta_{mt} \). This solution to the diffusion equation is valid 50 \( \mu \)s after the current is stopped and assumes semi-infinite one-dimensional diffusion, linear charge-transfer kinetics, negligible non-faradaic current due to double-layer charging, and solubility of O and R in either the electrolyte or the electrode. Care was taken in the experimental design and procedures to ensure that each of the assumptions used in the derivation remained valid (see Ref. 14 for in-depth discussion).

Each galvanostatic pulse had a duration of 0.5 s and consisted of three steps:
1. OCP step: \( I = 0 \),
2. transient step: \( I = I_p \), and
3. relaxation step: \( I = 0 \). After a two-minute rest period, the next pulse was initiated. Each sequence consisted of cathodic and anodic current steps of two different magnitudes. Two galvanostatic pulse sequences were performed, separated by a one-hour constant-potential hold. To test if the order of pulses affected the results the set of four pulses was repeated and the order of pulses changed in the second sequence.

### Results and Discussion

**Thermodynamic behavior.**—The OCP after coulometric titrations, \( E_{cell} \), was converted to the potential vs. the standard state (Mg(\( f \)) and Li(\( f \)) respectively), \( E_{WE} \), via the following relationship

\[
E_{WE} = E_{cell} + E_{REF},
\]

where \( E_{REF} \) is determined for the Mg-Sb system from experimental data given in Table S1 and for the Li-Bi system from data reported by Weppner and Huggins.\(^{15}\)

The resulting values exhibit good agreement to those measured during emf tests (i.e. with chemical, instead of electrochemical, formation of the alloys) (Figure 3). This suggests minimal non-faradaic transport of the itinerant ion.

**Cyclic voltammetry.**—Cyclic voltammograms at the tungsten and liquid electrodes in both the Mg-Sb and Li-Bi three-electrode cells are shown in Figure 4. Deposition at the alloying electrode occurs at a higher potential than pure metal deposition due to the decrease in activity of the itinerant species A in A-B alloys. In contrast, an inert electrode shows negligible faradaic processes over the same potential range.

**Exchange current density measurements.**—The exchange current densities of electrochemical alloying/de-alloying at liquid Mg-Sb and Li-Bi electrodes of varying composition were determined using the galvanostatic pulse method described in Galvanostatic transients section. Overpotential transients were corrected for the uncompensated resistance. Linear regression was performed on each \( \eta \) vs \( t^{1/2} \) trace and the exchange current density calculated from the intercept \( \eta_{0} \) according to Equation 4. Data for which the \( R^2 \) values were greater than 0.97 were included in the analysis.\(^{16}\) Representative data are presented in Figure 5.

The reproducibility of the transients within sequences was good; however, agreement between sequences was less consistent and thus an average \( j_0 \) was calculated for the cathodic and anodic pulses before and after the rest period. Anodic transients exhibited more curvature and less reproducibility than cathodic pulses and are not included in the following discussion. The calculated exchange current densities at alloying electrodes of varying composition are shown in Figure 6.

**Error analysis.**—The uncertainty in the calculated value of the exchange current density arises from three main sources: (1) reproducibility of the measurements, (2) uncertainty in the measured parameters, and (3) uncertainty in the shape of the electrode surface at high temperature. The following sections discuss the magnitudes of each source of error.

---

*For \( x_{MgSb} = 0.12 \) this condition was relaxed to \( R^2 < 0.95 \) to enable inclusion of more than one transient.
The average exchange current density values for A deposition at A-B liquid alloy electrodes calculated from cathodic current pulses. Lines are fits of the data to \( j_0 = C a_{(A/B)}^n \). Error bars indicate the standard deviation for each sequence.

**Reproducibility.**—The error shown in Figure 6 is the standard deviation of the exchange current density values calculated from the cathodic pulses in a given sequence. The low values of \( \eta_{\text{m}} \) make \( j_0 \) values very sensitive to slight changes in the slope of the fitted line (e.g., \( \pm 0.1 \text{ mV} \sim 10% \) of \( \eta_{\text{m}} \)). The standard deviation ranges from 2–15% of \( j_0 \) for Mg-Sb alloys and 2–27% of \( j_0 \) for Li-Bi.

**Differential error analysis.**—The exchange current density is derived from measured parameters, and the error in those measurements propagates to the calculated value of \( j_0 \). Differential error analysis enables calculation of the propagated error. For each transient, the exchange current density is calculated according to

\[
 j_0 = \frac{RT I_p}{zF A \eta_{\text{m}}(0)}, \tag{7}
\]

where the error in the absolute temperature \( T (\Delta T = 2 \text{ K}) \), applied current \( I_p (\Delta I_p = 0.05 \text{ mA}) \), electrode surface area \( A (\Delta A = 5 \times 10^{-3} \text{ cm}^2) \), and the intercept of the fit line \( \eta_{\text{m}}(0) (\Delta \eta_{\text{m}} = 0.091 \text{ mV}) \), each contribute error to the calculation. From differential analysis the error in \( j_0 \) due to these measurement uncertainties is about \( \pm 1 \text{ A/cm}^2 \).

**Systematic error in surface area.**—The error in the surface area accounted for in the differential analysis (\( \Delta A \)) is solely due to measurement of the capillary diameter. However, the shape of the electrode in the liquid state is unknown and thus the value used for the calculation of current density is an estimate. The error in this estimate is taken to be \( \pm 0.02 \text{ cm}^2 \), which would shift the calculated \( j_0 \) values up or down by approximately 10% but does not affect the relative positions.

**Discussion.**—For values of \( j_0 \) as large as those found in the present study the question of measurability arises. One way to judge measurability, suggested by Nagy, is to assume that the \( \eta_{\text{m}} \) must be no more than 10 times the \( \eta_0 \) for the duration of the current pulse. For a pulse time of 0.2 s this gives a limit on \( j_0 \) of \( \sim 40 \text{ A/cm}^2 \) for Mg-Sb electrodes and \( \sim 80 \text{ A/cm}^2 \) for Li-Bi electrodes. The \( j_0 \) values for Li-Bi level off around 60 A/cm², which lends support to this analysis. Thus, although the values are large and exhibit substantial error, some conclusions may be drawn from the above results.

The exchange current density of Li alloying/de-alloying at Li-Bi liquid electrodes exhibits marked dependence on the lithium activity in the alloy. Interfacial kinetic theory predicts a dependence of the exchange current density on the activity of the reduced species of \( j_0 \sim a_{(A/B)}^n \) (Eq. 3). A fit of the cathodically determined values of \( j_0 \) to the power function \( j_0 = C a_{(A/B)}^n \) is shown in Figure 6, and the parameters are given in Table II. The Li-Bi electrochemical alloying reaction exhibits a transfer coefficient \( \alpha > 0.5 \), which indicates that the electrostatic state of the activated complex more closely resembles that of the reduced species than that of the oxidized species. Although it is unusual for a charge transfer reaction with a neutral reduced species to have \( \alpha > 0.5 \), this behavior may be due to the highly ionic character of Li-Bi alloys.

The exchange current density of Mg alloying/de-alloying at Mg-Sb liquid electrodes exhibits a much lower dependence on the magnesium activity in the alloy than is the case for Li at Li-Bi liquid electrodes. A similar fitting of the data gives \( \alpha < 0.2 \) and a much worse “goodness of fit” as indicated by the adjusted R² value. One explanation for the lack of dependence on \( a_{(Mg/Sb)} \) is that the rate-determining step may not involve the completely reduced Mg species. For deposition of liquid Mg at inert electrodes, Kiszta et al. suggest the rate-determining step is the first electron transfer Mg²⁺ + e⁻ → Mg⁺. If a similar mechanism and rate-determining step are assumed at the Mg-Sb electrode, the invariance of \( j_0 \) with \( a_{(Mg/Sb)} \) is expected.

**Conclusions**

The measurements made in the present study suggest that the charge-transfer reactions for both Mg at Mg-Sb (660 °C) and Li at Li-Bi (450 °C) are very rapid so as to have negligible impact on the LMB cell performance.

**Acknowledgments**

We acknowledge financial support from Total, S.A.

**References**

1. H. Kim, D. A. Boysen, J. M. Newhouse, B. L. Spatocco, B. Chung, P. J. Burke, D. J. Bradwell, K. Jiang, A. A. Tomaszowska, K. Wang, W. Wei, L. A. Ortiz, S. A. Barriga, S. M. Pozeau, and D. R. Sadoway, “Liquid Metal Batteries: Past, Present, and Future,” Chem. Rev., 113 (3), 2075 (2013).
2. H. Gerischer, “Mechanism of electrolytic deposition and dissolution of metals,” Anal. Chem., 31, 3339 (1959).
3. K. F. Vetter, Electrochemical Kinetics: Theoretical and Experimental Aspects, New York: Academic Press, 1967.
4. Y. Castillero, M. R. Bermejo, P. D. Arocas, F. De la Rosa, and E. Barrado, “Electrode Reaction of Cerium into Liquid Bismuth in the Eutectic LiCl-KCl,” Electrochemistry Today, 73, 636 (2005).
5. Y. Castillero, M. R. Bermejo, P. D. Arocas, A. M. Martinez, and E. Barrado, “The electrochemical behaviour of the Pr(III)/Pr redox system at Bi and Cd liquid electrodes in molten eutectic LiCl-KCl,” J. Electroanal. Chem., 579, 343 (2005).
6. A. Kizza, “The Kinetics of the Sodium Electrode Reaction in Molten Sodium Chloride,” J. Electrochem. Soc., 142, 1035 (1995).
7. E. J. Cairns, C. E. Crouthamel, A. K. Fischer, M. S. Foster, J. C. Hesson, C. E. Johnson, H. Shimotake, and A. D. Tewbaugh, “Galvanic cells with fused-salt electrolytes,” Argonne National Laboratory, Argonne, Illinois, 1967.
8. D. Bradwell, H. Kim, A. H. C. Sirk, and D. R. Sadoway, “Magnesium-antimony liquid metal battery for stationary energy storage,” J. Am. Chem. Soc., 134, 1895 (2012).
9. H. Kim, D. A. Boysen, T. Ouchi, and D. R. Sadoway, “Cadmium-bismuth electrodes for large-scale energy storage (liquid metal batteries),” J. Power Sources, 241, 239 (2013).
10. T. Ouchi, H. Kim, X. Ning, and D. R. Sadoway, “Cadmium-Antimony Alloys as Electrodes for Liquid Metal Batteries,” J. Electrochem. Soc., 161(12), A1898 (2014).
11. K. Wang, K. Jiang, B. Chung, T. Ouchi, P. J. Burke, D. A. Boysen, D. J. Bradwell, H. Kim, U. Muecke, and D. R. Sadoway, “Lithium-antimony-lead liquid metal battery for grid-level storage,” Nature, 514(7522), 348 (2014).
12. X. Ning, S. Phadke, B. Chung, H. Yin, P. Burke, and D. R. Sadoway, “Self-healing Li-Bi liquid metal battery for grid-scale energy storage,” J. Power Sources, 275, 370 (2015).
13. A. J. Bard and L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications, 2nd ed. John Wiley & Sons, Inc., 2001.
14. J. M. Newhouse, Modeling the Operating Voltage of Liquid Metal Battery Cells, Massachusetts Institute of Technology, 2014.
15. W. Wepner and R. A. Huggins, “Thermodynamic Properties of the Intermetallic Systems Lithium-Antimony and Lithium-Bismuth,” J. Electrochem. Soc., 125, 714 (1978).
16. Z. Nagy, “D. C. Relaxation Techniques in Electrode Kinetics,” in *Modern Aspects of Electrochemistry*, vol. 21, R. R. Adzic, R. E. White, J. O. Bockris, and B. E. Conway, Eds., Plenum Press, 1990, p. 137.

17. G. Steinleitner, W. Freyland, and F. Hensel, “Electrical conductivity and excess volume of the liquid alloy system Li-Bi,” *Ber. Bunsenges. Phys. Chem.*, 79, 1186 (1975).

18. A. Kisza, J. Kazmierczak, B. Borresen, G. M. Haarberg, and R. Tunold, “Kinetics and Mechanism of the Magnesium Electrode Reaction in Molten MgCl2-NaCl Binary Mixtures,” *J. Electrochem. Soc.*, 144, 1646 (1997).

19. J. Sangster and A. D. Pelton, “The Bi-Li (Bismuth-Lithium) system,” *JPE*, 12, 447 (1991).

20. M. S. Foster, S. E. Wood, and C. E. Crouthamel, “Thermodynamics of Binary Alloys. I. The Lithium-Bismuth System,” *Inorg. Chem.*, 3, 1428 (1964).

21. M. L. Saboungi, J. Marr, and M. Blander, “Thermodynamic properties of a quasi-ionic alloy from electromotive force measurements: The LiPb system,” *J. Chem. Phys.*, 68, 1375 (1978).

22. W. Gasior and Z. Moser, “Thermodynamic study of liquid lithium-lead alloys using the emf method,” *J. Nucl. Mater.*, 294, 7783 (2001).

23. R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, and K. K. Kelley, *Selected Values of the Thermodynamic Properties of the Elements*, Metals Park, OH: American Society for Metals, 1973.