# Recycling ZnTe, CdTe, and Other Compound Semiconductors by Ambipolar Electrolysis

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ⓢ Supporting Information

ABSTRACT: The electrochemical behavior of ZnTe and CdTe compound semiconductors dissolved in molten $ZnCl_2$ and equimolar $CdCl_2-KCl$, respectively, was examined. In these melts dissolved Te is present as the divalent telluride anion, Te^{2-}, which was found able to be converted to elemental metal by electrochemical oxidation at the anode. $ZnTe-ZnCl_2$ melts were studied at 500 °C by standard electrochemical techniques. On the basis of these results, electrolysis was performed, resulting in the simultaneous extraction of phase-pure liquid Zn at the cathode and phase-pure liquid Te at the anode. This new process, involving the simultaneous deposition of liquid metals at electrodes of opposite polarity,

is termed herein as ambipolar electrolysis. A melt consisting of CdTe dissolved in equimolar $CdCl_2-KCl$ was processed by ambipolar electrolysis, resulting in the production of liquid Cd at the cathode and liquid Te at the anode. Ambipolar electrolysis could enable new approaches to recycling compound semiconductors and semiconductor devices, such as CdTe solar cells.
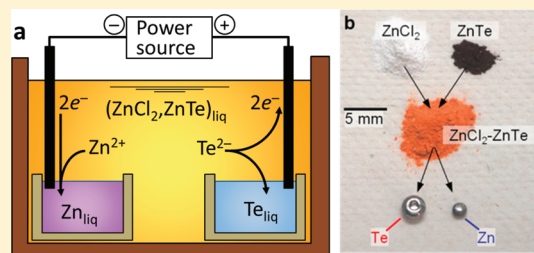
I. INTRODUCTION

Cadmium telluride (CdTe) has become a dominant material in thin film photovoltaic (PV) solar cell technology.[1] However, the toxicity of Cd and the scarcity of Te have raised concerns about the long-term prospects for broad-scale deployment of the compound.[2] Replacement materials, such as ZnTe, have been investigated; however, the scarcity of Te remains an issue. To address these concerns, mandatory recycling has been proposed,[3] but current processes involve multiple steps and ultimately produce a mixed-metal product that must be still further refined.[4] Here we show that a compound semiconductor, such as CdTe or ZnTe, can be dissolved in a molten salt bath and decomposed by electrolysis into its two elemental components which deposit as liquid metals onto electrodes of opposite polarity, a new process herein referred to as ambipolar electrolysis (AE). While the deposition of a liquid metal onto a cathode is standard practice, simultaneous anodic deposition of another liquid metal remains an area that has not received attention. Extraction of the two metal components as liquids at separate electrodes makes AE a one-step, continuous process for treating compound semiconductor waste. This process could be used as a critical step in recycling spent solar cells or in the reprocessing of compound semiconductors in other applications.[5] AE has been demonstrated in two distinct systems: ZnTe dissolved in molten $ZnCl_2$ at 500 °C and CdTe dissolved in equimolar molten $CdCl_2-KCl$ at 500 °C. $ZnTe-ZnCl_2$ melts were subjected to electrochemical characterization, and their electrolysis resulted in the production of phase-pure liquid metallic Zn and liquid

metallic Te at the cathode and anode, respectively. Similarly, electrolysis of CdTe resulted in the successful simultaneous deposition of liquid Cd and liquid Te at the cathode and anode, respectively. To the best of our knowledge, this paper describes the first demonstration of simultaneous electrodeposition of two liquid metals at electrodes of opposite polarity. Furthermore, this process offers the real possibility of reducing the cost of solar cell production through an effective approach to recycling.

AE represents a new form of molten salt electrolysis, which has long been the standard method for industrial-scale production of reactive metals, such as aluminum (Al) and magnesium (Mg).[6,7] In conventional electrolysis, the passage of electric current through a molten salt electrolyte results in the deposition of liquid metal at the cathode and generates a nonmetal, typically a gas, at the anode. For example, the electrolysis of $MgCl_2$ dissolved in a melt comprising KCl, NaCl, and $CaCl_2$ results in the production of liquid Mg at the cathode and chlorine (Cl_2) gas at the anode. Interestingly, some semiconducting intermetallic compounds exhibit solubility in molten salts exceeding that of their constituent elements,[8,9] suggesting that the dissolved electronegative element, commonly a metalloid, possesses a negative formal charge.[10] While metal/metalloid ions usually have a positive formal charge, there are instances where the contrary has been observed. For instance, liquid cesium–gold (Cs–Au) alloys at 600 °C at near-equimolar proportions demonstrate ionic

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behavior.[12] The large difference in electronegativity between the two metals results in electron transfer between them and formation of a melt comprising Cs^+ and Au^-. Interestingly, ZnTe (a semiconductor with a band gap of ~2.2 eV and T_{mp} = 1295 °C [13]) has been shown to be highly soluble in molten $ZnCl_2$ (>10 mol % at 700 °C [8]). This is much greater than the solubility of pure Zn in liquid $ZnCl_2$ (<2 mol % at 700 °C [9]), suggesting that ZnTe may dissolve as Zn^{2+} and Te^{2-}. Thus, tellurium (Te), which upon melting changes from a small band gap semiconductor to a poor metal,[14] can be extracted as a liquid metal by the oxidation of Te^{2-} at the anode with the reduction of Zn^{2+} to liquid Zn metal, the compensating reaction at the cathode. Similarly, CdTe has been found to be soluble in molten $CdCl_2-KCl$,[8] suggesting that the analogous reaction, involving the cathodic deposition of Cd instead of Zn, is possible. Only limited work has been performed on the anodic deposition of metals, demonstrating the stability of Te^{2-} ions in certain molten salts,[10] anodic deposition of solid powdered Te from a room temperature molten salt (ionic liquid),[11] and the evolution of gaseous Te as a byproduct of Cu electrorefining.[15] By contrast, AE is distinctly different from cathodic co-deposition of CdTe as has been widely studied for solar applications.[16,17] Therefore, anodic metal deposition remains a sparsely studied area and, to the best of our knowledge prior to this study, had not yet found a useful application. In the present study, the widely unknown practice of anodic metal deposition and the standard practice of cathodic metal deposition have been combined into a single process that could be exploited for semiconductor recycling. The passage of current through a molten salt bath in which is dissolved a compound semiconductor can cause its decomposition and attendant simultaneous deposition of two metals onto separate electrodes, each of opposite polarity. We name this phenomenon ambipolar electrolysis (AE), referring to the electrolytic production of distinct liquid metal products at the positively and negatively polarized electrodes. Here we demonstrate AE of ZnTe dissolved in molten $ZnCl_2$ and CdTe dissolved in equimolar $CdCl_2-KCl$. The molten salts containing dissolved compound semiconductors were subjected to electrochemical characterization which informed the processing conditions for the galvanostatic production of the constituent liquid elements.

II. EXPERIMENTAL SECTION

Due to the hygroscopic nature of these salts, great care was taken to ensure minimal exposure to moisture. In an argon-filled glovebox, a fused quartz crucible was charged with powders of the compound semiconductor and/or the chloride salt(s) and sealed inside a stainless steel vessel. For the ZnTe experiments, high-purity $ZnCl_2$ (ultradry, 99.999%, Alfa-Aesar) and high-purity ZnTe (99.99%, Alfa-Aesar) were used; for the CdTe study, reagent grade $CdCl_2$ (99%, Alfa-Aesar), KCl (99%, Alfa-Aeasar), and CdTe (99.999%, Alfa-Aesar) were used.

The salts were vacuum-dried in a sealed test vessel for 12 h at 80 °C and then for 4 h at 240 °C. Electrochemical experiments were performed under an argon atmosphere in a cell fitted with a glassy carbon disk working electrode (WE) with an area of 3.07 mm², a glassy carbon rod counter electrode (CE), and a brass (Cu−Zn alloy) rod reference electrode (RE). Electrolysis experiments were performed using two glassy carbon rod electrodes each fitted with a mullite cup capable of retaining the electrodeposited metal. Electrochemical peak current measurements were performed to ensure that the compound semiconductor had completely dissolved in the melt prior to performing characterization measurements (Supporting Information Figure 1a,b).

Electrochemical measurements (cyclic voltammetry (CV), electrochemical impedance spectroscopy, and galvanostatic electrolysis) were performed using a PARSTAT model 2273 potentiostat/galvanostat controlled by PowerSuite 2.58 software. In the ZnTe studies, potential measurements were made with respect to the brass RE but are reported with respect to the $Zn^{2+}|Zn$ potential (Supporting Information Figure 2a,b). Materials analysis was performed using two techniques: energy-dispersive X-ray spectroscopy (EDS) controlled by EDS2004 software, as part of a Leo 438VP scanning electron microscope (SEM) operated at 20 kV, and X-ray diffraction (XRD) analysis performed using a Bruker D8 multipurpose diffractometer with a GADDS 2D area detector, operated at 40 keV and 40 mA with a copper anode and a 0.5 mm collimator. Bulk chemical analyses were performed by Luvak, Inc., using direct coupled plasma optical emissions spectroscopy, ion selective electrodes, and inert gas fusion analysis. Further information on the experimental setup can be found in the Supporting Information.

III. RESULTS AND DISCUSSION

ZnTe dissolution and dissociation in molten $ZnCl_2$ was first examined electrochemically. Cyclic voltammetry was performed at 500 °C on pure molten $ZnCl_2$ (Figure 1a) and $ZnCl_2$ melt containing 0.5 mol % ZnTe (Figure 1b), which is below the expected solubility limit of ZnTe in this solvent (~2 mol % at 500 °C[8]). The voltammogram of $ZnCl_2$ exhibits the electrical signatures of (1) liquid metal deposition ($Zn^{2+} + 2e^- \rightarrow Zn$), (2) metal stripping ($Zn \rightarrow Zn^{2+} + 2e^-$), and (3) gas evolution ($2Cl^- \rightarrow Cl_2 + 2e^-$). Cl_2 evolution occurs beyond the potential, $E \approx 1.6$ V (vs Zn/Zn^{2+}), in agreement with the theoretical dissociation potential of $ZnCl_2$ ($\Delta E = 1.57$ V), as calculated from the Gibbs free energy of formation of the pure compound.[18] The voltammogram of a melt containing 0.5 mol % ZnTe (Figure 1b) exhibits an additional set of peaks near 0.6 V attributed to (4) anodic deposition of a liquid metal ($Te^{2-} \rightarrow Te + 2e^-$) and (5) stripping of the same on the cathodic reverse sweep ($Te + 2e^- \rightarrow Te^{2-}$). These new peaks occur at a potential of ~0.56 V, which is the value of the dissociation potential of pure ZnTe at 500 °C, as calculated from the Gibbs free energy of the pure compound.[19] Note that the Cl_2 evolution potential (1.6 V) greatly exceeds the potential associated with the newly observed peak, indicating that current passed at potentials in the range of the new peak (0.4−0.8 V) is not attributable to Cl_2 evolution. CV scans sweeping to successively more anodic potentials (Figure 1c) indicate that the reverse stripping reaction occurs only when Te has first been deposited. Furthermore, the reverse peak is much sharper than the forward peak, consistent with the production and subsequent electrochemical stripping of the pure element.[20] CV scans at different sweep rates (Figure 1d) show an almost linear relationship between peak current, i_p, and the square root of the sweep rate, $\nu^{1/2}$ (Figure 1d, inset); however, the slight shift in the peak potential, E_p (E at i_p), with ν, even after compensation for IR drop across the electrolyte, suggests that the Te deposition reaction is likely quasireversible.

Further evidence associating the peak near 0.6 V with the anodic deposition of Te can be found in the linear variation of peak current density with ZnTe concentration. CVs were recorded for $ZnCl_2$ melts containing 0.1, 0.5, 1.0, and 1.4 mol % ZnTe (Figure 2a). These concentrations corresponded to molar concentrations of (0.168, 0.842, 1.69, and 2.37) × 10^{-4} mol cm^{-3}, respectively, on the basis of the temperature-dependent liquid density of $ZnCl_2$[21] and solid ZnTe. As with the data in Figure 1d, i_p was observed to vary linearly with $\nu^{1/2}$ (Figure 2b).
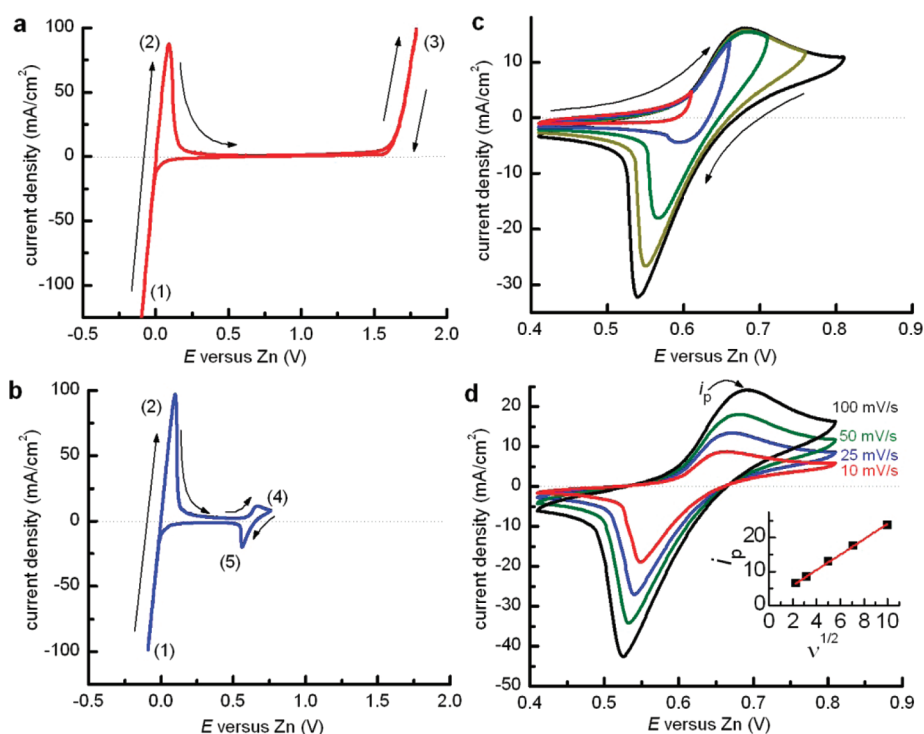
Figure 1. Electrochemical scans at 500 °C illustrating simultaneous cathodic and anodic deposition of two liquid metals: (a) cyclic voltammogram of pure molten $ZnCl_2$ indicating liquid Zn deposition (1), Zn stripping (2), and Cl_2 gas evolution (3); (b) cyclic voltammogram of $ZnCl_2$ containing ZnTe, indicating liquid Te deposition (4) and Te stripping (5); (c) scans swept to successively more anodic potentials demonstrate that the Te stripping peak occurs only when scans exceed 0.6 V; (d) peak current density, i_p, of the $Te^{2-} \rightarrow Te + 2e^-$ waves exhibiting the expected linear dependence on scan rate, $\nu^{1/2}$ (inset). Cyclic voltammograms were measured at sweep rates of 20 (a, b), 50 (c), and 10, 25, 50, and 100 mV/s (d), respectively. ZnTe concentration was 0.5 mol % (b–d).
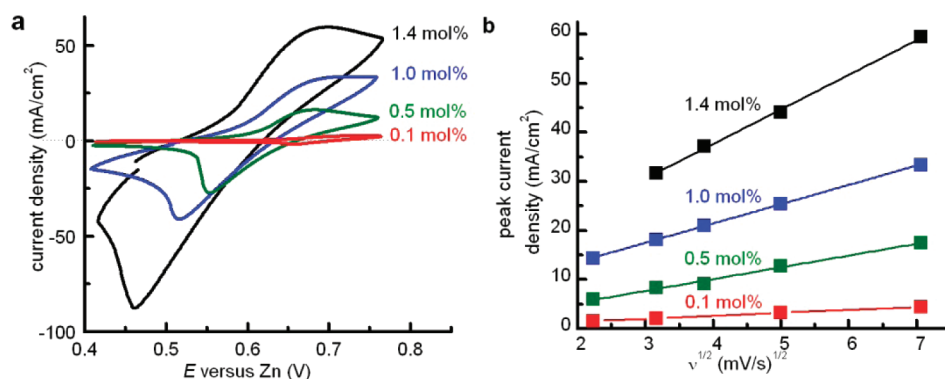

Figure 2. Effect of ZnTe concentration at 500 °C: (a) cyclic voltammogram of the $(Te^{2-} \rightarrow Te + 2e^-)$ peak at various concentrations (ν = 50 mV/s); (b) peak current density, i_p, as a function of scan rate, $\nu^{1/2}$, for melts containing 0.1, 0.5, 1.0, and 1.4 mol % ZnTe.

To reveal their electrical properties ZnTe-bearing melts were characterized by stepped potential measurements to garner information about the electronic conductivity (Supporting Information Figure 3a,b) and electrochemical impedance spectroscopy to determine the value of the total electrical (ionic and electronic) conductivity (Supporting Information Figure 4a). The electronic transference number, t_{e-}, which is the fraction of charge passed due to the flow of electrons vs to the combined flow of ions and electrons, was determined to be between 0.03 and 0.3%, indicating that the dominant mode of electrical conduction in these melts is ionic.

The charge-transfer resistance (R_{ct}) of the $Zn^{2+} + 2e^- \leftrightarrow Zn$ reaction was determined by electrochemical impedance spectroscopy of a thin layer of elemental zinc electrodeposited onto a glassy carbon electrode. During the impedance scans the electrode was held at 0 V vs $Zn|Zn^{2+}$. A characteristic semicircle was observed, and the value of the charge-transfer resistance was calculated to be 0.04 Ω cm^2, corresponding to an exchange current density of 800 mA cm^{-2} (Supporting Information Figure 4a).[20] This is far greater than the exchange current density of H_2 on smooth Pt $(0.35–0.9$ mA $cm^{-2})$,[22] which is considered to be a fast reaction. Attempts to measure R_{ct} for the $Te + 2e^- \leftrightarrow Te^{2-}$ reaction failed, possibly due to poor wetting of the working electrode by liquid Te.
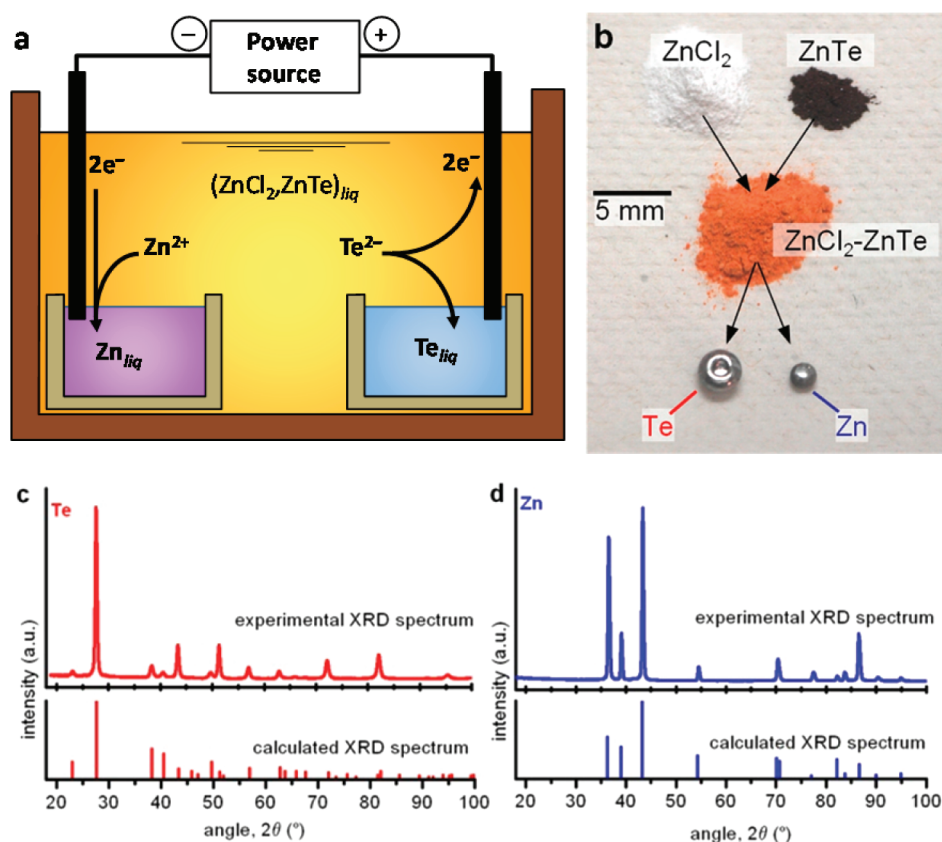
Figure 3. Ambipolar electrolysis of Zn and Te: (a) schematic of the electrolysis cell (as current passes, Te and Zn are simultaneously electrodeposited as liquid metals on electrodes of opposite polarity); (b) mixture of pure powdered $ZnCl_2$ (white, top left) melted with ZnTe (deep burgundy, top right), producing a mixed melt (orange, center) (constant-current electrolysis of a $ZnCl_2-ZnTe$ melt produced two metal products, Te (bottom left) at the anode and Zn (bottom right) at the cathode; the Te deposit collected around the end of the glassy carbon current lead and produced a depression when the rod was removed); (c) XRD spectrum of metal deposited at the anode (top) and calculated spectrum of Te metal (bottom) (the deposit was phase-pure Te); (d) XRD spectrum of metal deposited at the cathode (top) and calculated spectrum of Zn metal (bottom) (deposit was phase-pure Zn).

On the strength of these electrochemical findings, AE cells were constructed, capable of producing and collecting Zn and Te liquid metal deposits (Figure 3a). Galvanostatic (constant current) electrolysis was performed on a $ZnCl_2$ melt containing 1.0 mol % ZnTe. The cell was operated at 3 mA ($i \approx$ 15 mA cm^{-2}) for 85 h during which time the cell potential varied from 0.5 to 0.8 V. At potentials exceeding 0.8 V, the formation of $TeCl_2$, $TeCl_4$, and Cl_2 gas was anticipated. In situ measurements of t_{e-} were taken concurrently during electrolysis experiments and the electronic conductance of the electrolyte did not markedly change throughout the course of the experiment. Electrodeposits (Figure 3b) were removed from the melt for analysis by EDS and XRD (Figure 3c,d) and were determined to be phase-pure Zn at the cathode and phase-pure Te at the anode. Bulk chemical analysis was also performed on the metallic products from a separate electrolysis experiment under similar conditions. The Zn product was >98% pure, with Fe as the dominant impurity (1.8 wt %). The likely source of the Fe impurity is the steel electrode lead. The Te product was >99.8% pure, with Zn as the dominant impurity at 0.15 wt %. The complete compositional analysis is included in Supporting Information Table 1. These purity levels meet metallurgical grade specification; however, subsequent purification steps will be required to make this metal useful in solar or electronic applications.

Coulombic efficiency, based on the ratio of the mass of deposited product (0.16 g of Zn and 0.42 g of Te) to amount of electrical charge passed during electrolysis (920 C), was determined to be 51% for Zn and 67% for Te, respectively. Inefficiencies are possibly due to the dissolution of the metal into the salt or incomplete coalescence of metal droplets with the bulk deposit, as evidenced by the presence of a metal film on the crucible and on the electrode sheaths. Poor wetting of Te on the electrode was evident upon solidification. Previous work on the electrodeposition of Zn at 500 °C from molten $ZnCl_2-NaCl$ measured faradaic efficiencies exceeding 90%,[23] with most of the loss attributed to melt agitation from Cl_2 evolution leading to back-reaction with Zn droplets. This suggests that the current efficiency of the AE cell could be improved with a modified cell design and by optimization of electrolyte composition.

AE was also performed at 500 °C on an equimolar melt of $CdCl_2-KCl$ containing 1 mol % CdTe. Galvanostatic electrolysis was performed at 15 mA over a period of 105 h. The cell voltage drifted from 0.56 to 0.65 V, which is near the expected dissociation potential of CdTe (0.51 V[24]). Electrolysis resulted in the deposition of liquid Cd (1.5 g) and liquid Te (1.2 g), corresponding to cathodic and anodic Coulombic efficiencies of 45 and 40%, respectively. The deposits were phase-pure, as determined by SEM/EDS and XRD analyses (Supporting Information Figure 5). Bulk sample chemical analysis indicated that

the Cd product was >99.9% pure (with 0.048 wt % Ni as the largest impurity, and <0.002% Te) and that the Te product was >99% pure (with 0.78 wt % Cd as the largest impurity). The complete bulk analysis is included in Supporting Information Table 1.

IV. CONCLUSIONS

A single-step, electrochemical approach to recycling compound semiconductor materials has been proposed, and its proof of principle has been demonstrated. Electrolysis of ZnTe−ZnCl$_2$ melts resulted in the production of phase-pure liquid Zn and liquid Te. Similarly, electrolysis of CdTe dissolved in molten equimolar CdCl$_2$−KCl resulted in the deposition of phase-pure liquid Cd and liquid Te. Further study is required to investigate alternative electrolytes to improve cell performance and evaluate the role of impurities and other solar cell constituents in the feedstock. In the near term, this process could be directly applied to recycling CdTe manufacturing waste which represents 10−30% of the total CdTe consumed in the production of CdTe PVs. Eventually, AE could play a critical role in recycling these resource-limited and hazardous compounds, enabling broader scale deployment of thin-film solar cell technologies and lowering the cost of compound semiconductor devices.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Text describing the experimental setup, figures showing the ZnTe dissolution in ZnCl$_2$, brass rod reference electrode calibration in molten ZnCl$_2$, DC stepped potential for electronic conductivity measurements, AC impedance response, and ambipolar electrolysis of CdTe, and a table listing bulk compositional analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

■ REFERENCES

(1) Poortmans, J.; Arkhipov, V. *Thin film solar cells: Fabrication, characterization and applications*; John Wiley & Sons: New York, 2006.

(2) Aberle, A. *Thin Solid Films* **2009**, *517*, 4706–4710.

(3) Larsen, K. renewableenergyfocus.com, 2009.

(4) Fthenakis, V. *Energy Policy* **2000**, *28*, 1051–1058.

(5) Schlesinger, T.; Toney, J.; Yoon, H.; Lee, E.; Brunett, B.; Franks, L.; James, R. *Mater. Sci. Eng., R* **2001**, *32*, 103–189.

(6) Grjotheim, K.; Kvande, H. *Introduction to aluminium electrolysis*, 2nd ed.; Aluminium-Verlag: Dusseldorf, Germany, 1993.

(7) Kipouros, G.; Sadoway, D. *Adv. Molten Salt Chem.* **1987**, *6*, 127–209.

(8) Rodionov, Y. I.; Klokman, V. R.; Myakishev, K. G. *Russ. J. Inorg. Chem.* **1972**, *17*, 440–443.

(9) Kerridge, D.; Tariq, S. *J. Chem. Soc. A* **1967**, 1122–1125.

(10) Gruen, D. M.; McBeth, R. L.; Foster, M. S.; Crouthamel, C. E. *J. Phys. Chem.* **1966**, *70*, 472–477.

(11) Jeng, E.; Sun, I. *J. Electrochem. Soc.* **1997**, *144*, 2369–2374.

(12) Hoshino, H.; Schmutzler, R. W.; Hensel, F. *Phys. Lett. A* **1975**, *51*, 7–8.

(13) Glazov, V.; Pavlova, L. *High Temp.* **2001**, *39*, 68–74.

(14) Bichara, C.; Raty, J.; Gaspard, J. *Phys. Rev. B* **1996**, *53*, 206–211.

(15) Ward, R. G.; Hoar, T. P. *J. Inst. Met.* **1961**, *90*, 6–12.

(16) Dergacheva, M.; Statsyuk, V.; Fogel, L. *J. Electroanal. Chem.* **2005**, *579*, 43–49.

(17) Ham, S.; Choi, B.; Myung, N.; de Tacconi, N.; Chenthamarakshan, C.; Rajeshwar, K.; Son, Y. *J. Electroanal. Chem.* **2007**, *601*, 77–82.

(18) Bard, A.; Faulkner, L. *Electrochemical methods: Fundamentals and applications*, 2 ed.; John Wiley & Sons: New York, 2001.

(19) Barin, I.; Knacke, O. *Thermodynamic properties of inorganic substances*; Springer-Verlag: Berlin, New York, 1973.

(20) Pletcher, D. *Instrumental methods in electrochemistry*; Horwood: Chichester, U.K., 2001.

(21) Janz, G. J. *Molten salts handbook*; Academic: New York, 1967.

(22) Kibler, L. A. *ChemPhysChem* **2006**, *7*, 985–991.

(23) Fray, D. *J. Appl. Electrochem.* **1973**, *3*, 103–112.

(24) Alikhanian, A.; Guskov, V.; Natarovskii, A.; Kovalenko, V. *Inorg. Mater.* **2003**, *39*, 234–239.

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