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Recycling ZnTe, CdTe, and other compound semiconductors by ambipolar electrolysis

David J. Bradwell[†], Sebastian Osswald[‡], Weifeng Wei[†], Salvador A. Barriga[†], Gerbrand Ceder[†], Donald R. Sadoway^{†*}

[†]Department of Materials Science and Engineering, Massachusetts Institute of Technology, USA

*Corresponding author

Supporting Information Placeholder

ABSTRACT: The electrochemical behavior of ZnTe and CdTe compound semiconductors dissolved in ZnCl₂ and equimolar CdCl₂-KCl molten salts, respectively, was examined. Electrochemical results indicate that dissolved Te can exist in these molten salts with a 2- valence state, enabling it to be extracted anodically from the melt. ZnTe-ZnCl₂ melts were studied at 500 °C via standard electrochemical techniques. Based on these results, electrolysis was performed, resulting in the simultaneous extraction of phase pure liquid Zn at the anode and phase pure liquid Te at the cathode. This new process, involving the simultaneous deposition of liquid metals at electrodes of opposite polarity is referred to as ambipolar electrolysis. Ambipolar electrolysis was also performed on a melt consisting of CdTe dissolved in equimolar CdCl₂-KCl, resulting in the successful deposition of Cd and Te at the cathode and anode, respectively. Ambipolar electrolysis could enable new approaches to recycling compound semiconductors and semiconductor devices, such 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 their two elemental components which deposit as liquid metals onto electrodes of opposite polarity, a new process here-in referred to as ambipolar electrolysis (AE). While the deposition of a liquid metal onto a cathode is standard practice, anodic deposition of a liquid metal remains an area that has not received attention. By extracting the two metal components as liquids at separate electrodes, AE provides a one-step, continuous process from 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 ZnCl₂ at 500 °C, and CdTe dissolved in equimolar molten CdCl₂-KCl at 500 °C. ZnTe-ZnCl₂ 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. To the best of our knowledge, this paper describes the first demonstration of simultaneously electrodeposited liquid metals at electrodes of opposite polarity. Furthermore, this process offers the real possibility of reducing the cost of solar cell production through a cost 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 non-metal, 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 $600\text{ }^\circ\text{C}$ at near equimolar proportions demonstrate ionic behavior.¹¹ The large difference in electronegativity between the two metals results in electron transfer between them and formation of a melt comprising Cs^+ and Au^- ions. Interestingly, ZnTe (a semiconductor with a band gap of $\sim 2.2\text{ eV}$ and $T_{\text{mp}} = 1295\text{ }^\circ\text{C}$ ¹²) has been shown to be highly soluble in molten ZnCl_2 ($> 10\text{ mol}\%$ at $700\text{ }^\circ\text{C}$ ⁸). This is much greater than the solubility of pure Zn in liquid ZnCl_2 ($< 2\text{ mol}\%$ at $700\text{ }^\circ\text{C}$ 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,¹³ can be extracted as a liquid metal via oxidation of Te^{2-} at the anode while the compensating reaction will be the reduction of Zn^{2+} to liquid Zn metal at the cathode. Similarly, CdTe has been found to be soluble in molten $\text{CdCl}_2\text{-KCl}$,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), and the evolution of gaseous Te as a byproduct of Cu electrorefining.¹⁴ By contrast, AE is distinctly different than cathodic co-deposition of CdTe as has been widely studied for solar applications.^{15,16} Therefore, anodic metallic deposition remains a sparsely studied area, and to the best of our knowledge, 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 utilized in semiconductor recycling. By passing current through a molten salt bath containing a dissolved compound semiconductor, simultaneous deposition of two metals onto separate electrodes, each of opposite polarity, is possible. We name this phenomenon ambipolar electrolysis (AE), referring to the electrolytic production of distinct liquid metal products at both the positively and negatively polarized electrodes. Here we demonstrate AE of ZnTe dissolved in molten ZnCl_2 , and CdTe dissolved in equimolar $\text{CdCl}_2\text{-KCl}$. The molten salts were subjected to electrochemical characterization which informed the processing conditions for the galvanostatic production of the 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 glove box, 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 (ultra-dry, 99.999 %, Alfa-Aesar) and high purity ZnTe (99.99 %, Alfa-Aesar) were used; and for the CdTe study, reagent grade CdCl_2 (99 %, Alfa-Aesar), KCl (99 %, Alfa-Aesar), and CdTe (99.999 %, Alfa-Aesar) were used.

The salts were vacuum dried in a sealed test vessel for 12 h at $80\text{ }^\circ\text{C}$ and then for 4 h at $240\text{ }^\circ\text{C}$. 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 mm^2 , 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 fitted with a mullite cups capable of retaining the electrodeposited metal. Electrochemical peak current measurements were performed to ensure the compound semiconductor had completely dissolved in the melt prior to performing characterization measurements (Supp. Fig 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 related studies, potentials measurements were made with respect to the brass RE, but are reported with respect the $\text{Zn}^{2+}|\text{Zn}$ potential (Supp. Fig 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 analysis was 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 (Fig. 1a) and ZnCl_2 melt containing 0.5 mol% ZnTe (Fig. 1b), which is below the expected solubility limit of ZnTe (~ 2 mol% at 500 °C⁸). The cyclic voltammogram (CV) of ZnCl_2 exhibits the electrical signatures of (1) liquid metal deposition ($\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$), (2) metal stripping ($\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$), and (3) gas evolution ($2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$). 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.¹⁷ The CV of a melt containing 0.5 mol% ZnTe (Fig. 1b) exhibits an additional set of peaks near 0.6 V attributed to (4) anodic deposition of a liquid metal ($\text{Te}^{2-} \rightarrow \text{Te} + 2\text{e}^-$) and (5) stripping of same on the cathodic reverse sweep ($\text{Te} + 2\text{e}^- \rightarrow \text{Te}^{2-}$). 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 calcu-

lated from the Gibbs free energy of the pure compound.¹⁸ 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 V to 0.8 V) is not attributable to Cl_2 evolution. CV scans sweeping to successively more anodic potentials (Fig. 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.¹⁹ CV scans at different sweep rates (Fig. 1d) shows an almost linear relationship between peak current, i_p , and the square root of the sweep rate, $\nu^{1/2}$ (Fig. 1d inset); however, the slight shift in the peak potential, E_p (E at i_p), with ν , even after compensating for IR drop through 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 (Fig. 2a). These concentrations corresponded to molar concentrations of (0.168, 0.842, 1.69, and 2.37) $\times 10^{-4}$ mol cm^{-3} , respectively, based on the temperature dependent liquid density of ZnCl_2 ²⁰ and solid ZnTe. As with the data in Fig. 1d, i_p was observed to vary linearly with $\nu^{1/2}$ (Fig. 2b).

The electrical properties of ZnTe-bearing melts were characterized by stepped potential measurements to garner information about the electronic conductivity (Supp. Figs. 3a-b) and electrochemical impedance spectroscopy to investigate the total electrical (ionic & electronic) conductivity (Supp. Fig. 4a). The electronic transference number, t_{e-} , which is the fraction of charge passed due to the flow of electrons versus 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.

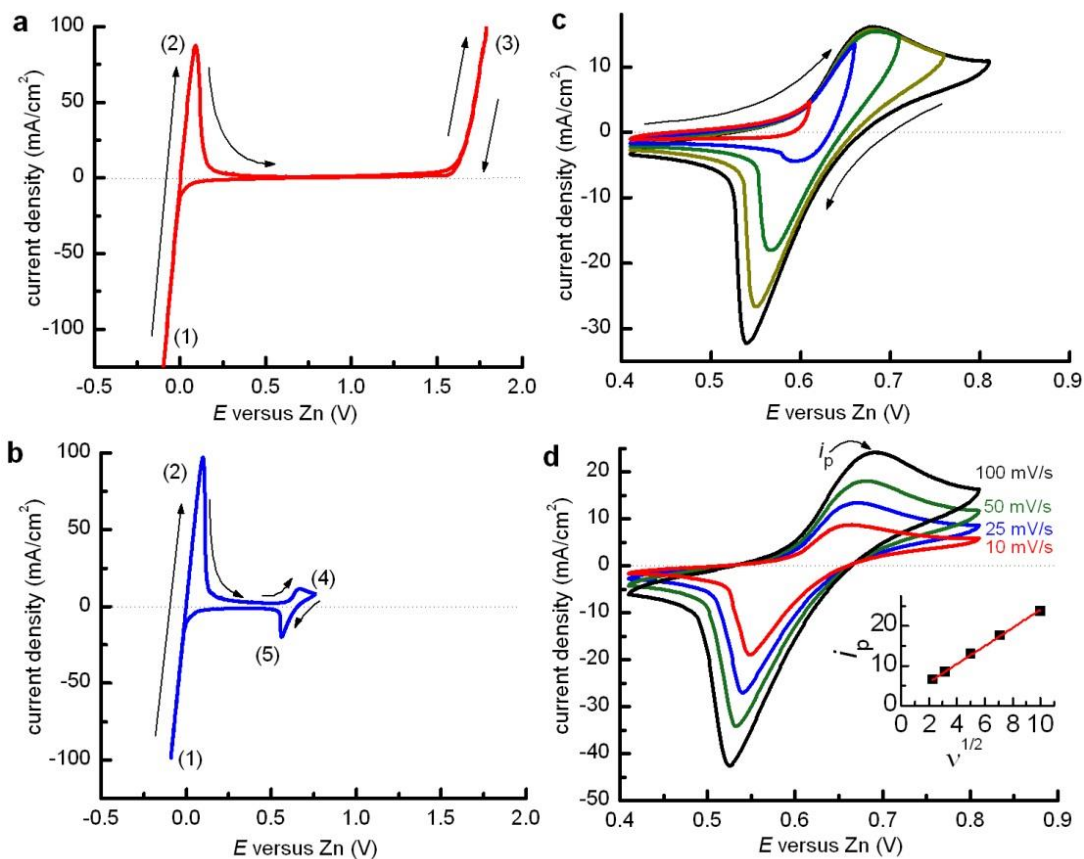


Figure 1. Electrochemical scans at 500 °C illustrating simultaneous cathodic and anodic deposition of two liquid metals. **a**, Cyclic voltammogram (CV) of pure molten ZnCl_2 indicating liquid Zn deposition (1), Zn stripping (2), and Cl_2 gas evolution (3). **b**, CV of ZnCl_2 containing ZnTe, indicating liquid Te deposition (4) and Te stripping (5). **c**, Scans swept to successively more anodic potentials demonstrate that the Te stripping peak only occurs when scans exceed 0.6 V. **d**, The peak current density, i_p , of the $(\text{Te}^{2-} \rightarrow \text{Te} + 2e^-)$ waves exhibit the expected linear relationship with scan rate, $v^{1/2}$ (inset). CVs were conducted at sweep rates of 20 mV/s (a,b), 50 mV/s (c), and 10, 25, 50, and 100 mV/s (d), respectively. ZnTe concentration was 0.5 mol% (b, c, and d).

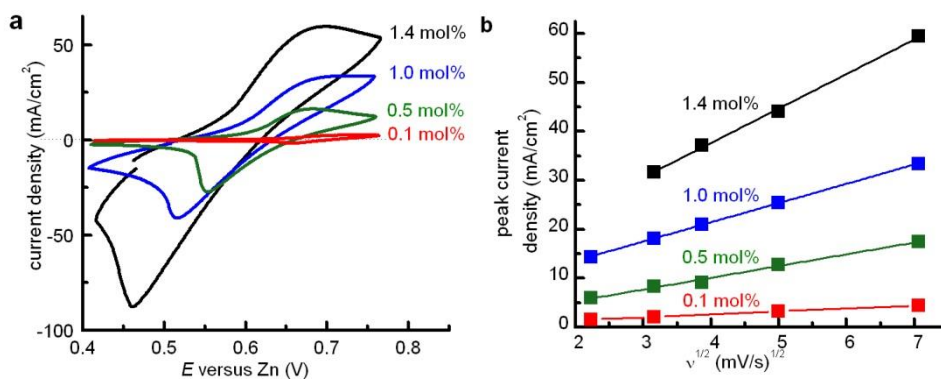


Figure 2. Effect of ZnTe concentration at 500 °C. **a**, CV of the $(\text{Te}^{2-} \rightarrow \text{Te} + 2e^-)$ peak at various concentrations ($v = 50$ mV/s). **b**, Peak current density, i_p , as a function of the $v^{1/2}$ for melts containing 0.1, 0.5, 1.0, and 1.4 mol% ZnTe.

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. The electrode was held at zero volts vs. $Zn|Zn^{2+}$ during the impedance scan. A characteristic semi-circle was observed, and the value of the charge-transfer resistance was calculated to be $0.04 \Omega \text{ cm}^2$, corresponding to an exchange current density of 800 mA cm^{-2} (Supp. Fig. 4a).¹⁹ This is far greater than the exchange current density of H_2 on smooth Pt (0.5 mA cm^{-2}),²¹ 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.

On the strength of these electrochemical findings, AE cells were constructed, capable of producing and collecting Zn and Te liquid metal deposits (Fig. 3a). Galvanostatic (constant current) electrolysis was performed on a $ZnCl_2$ melt containing 1.0 mol% ZnTe. The cell was operated at 3 mA ($i \approx 15 \text{ mA cm}^{-2}$) for 85 h during which time the cell potential varied from 0.5 V 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 (Fig. 3b) were removed from the melt for analysis by EDS and XRD (Fig. 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 Zn and 0.42 g 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 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 %, ²² 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 V to 0.65 V, which is near the expected dissociation potential of CdTe (0.51 V ²³). Electrolysis resulted in the deposition of liquid Cd (1.5 g) and liquid Te (1.2 g), corresponding to cathode and anodic coulombic efficiencies of 45 % and 40 %, respectively. The deposits were phase pure, as determined from SEM/EDS and XRD analyses (Supp. Fig 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 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.

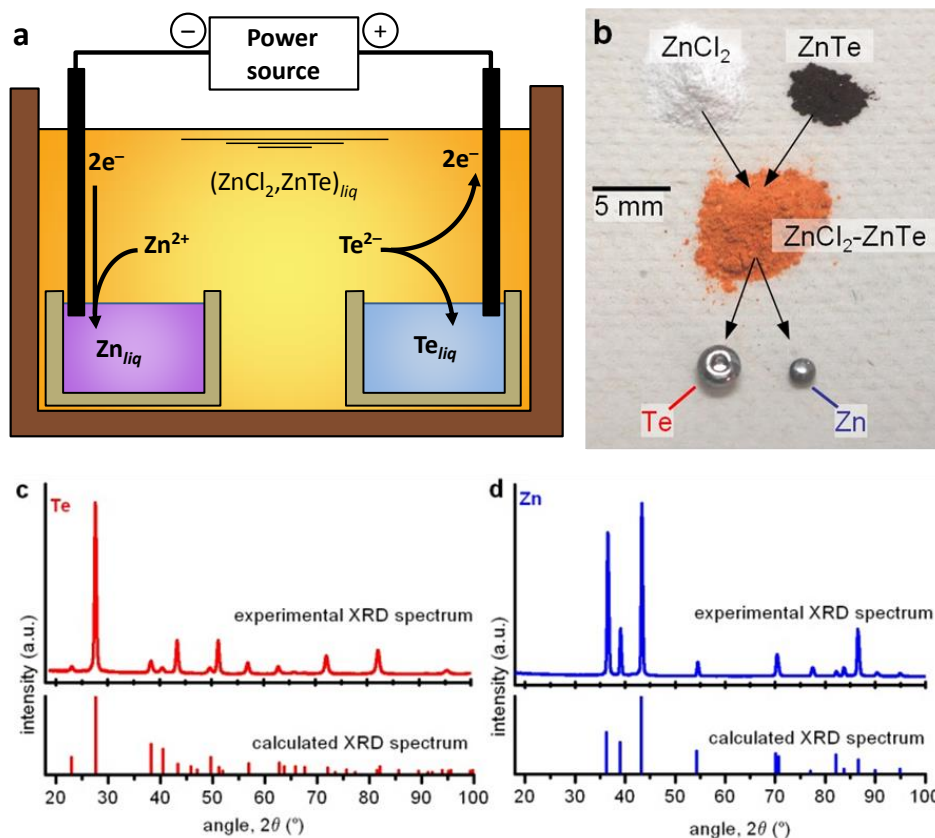


Figure 3. Ambipolar electrolysis of ZnTe. **a**, Schematic of the electrolysis cell. As current passes, Te and Zn are simultaneously electrodeposited as liquid metals on electrodes of opposite polarity. **b**, Pure powdered ZnCl₂ (white, top left) was mixed and melted with ZnTe (deep burgundy, top right), producing a mixed melt (orange, center). Constant current electrolysis of a ZnCl₂-ZnTe melt produced two metal products: Te (bottom left) at the anode and Zn (bottom right) at the cathode. The Te deposit was collected around the end of the glassy carbon current lead, and produced a depression when the rod was removed. **c**, Experimental XRD spectrum of metal deposited at the anode (top) and calculated spectrum of Te (bottom). Deposit was phase-pure Te. **d**, Experimental XRD spectrum of metal deposited at the cathode (top) and calculated spectrum of Zn metal (bottom). Deposit was phase-pure Zn.

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-ZnCl₂ melts resulted in the production of phase-pure Zn and Te. Similarly, electrolysis of CdTe dissolved in molten equimolar CdCl₂-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. Based on the results of this study, AE has been demonstrated as a simple recycling technique for CdTe and ZnTe compound semiconductors. In the near term, this process could be directly applied to recycling CdTe manufacturing waste which represents 10 % to

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 chemical, enabling broader scale deployment of thin film solar cell technologies and lowering the cost of compound semiconductor devices.

ASSOCIATED CONTENT

Supporting Information.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

* Room 4-217, 77 Massachusetts Ave., Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, USA

Present Addresses

*Current address: Naval Postgraduate School, Department of Physics, 833 Dyer Road, Bldg. 232, Room 110, Monterey, CA, 93943-5193, USA

Author Contributions

W.W. performed material analysis. G.C., D.S., and D.B. contributed to the conceptual development of this idea. S.O., W.W., and D.B. designed the study and performed the experiments. S.B. performed the CdTe electrolysis experiments. D.B. analyzed the results and wrote the original draft of the paper. D.S., W.W., and S.O. edited the original manuscript and revised it for submission. All authors discussed the results and commented on the paper.

Funding Sources

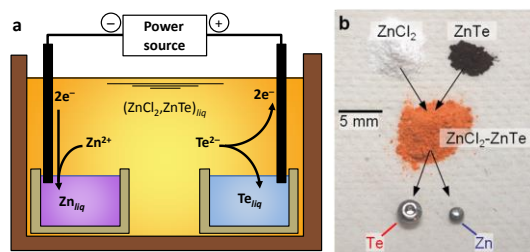
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SUPPORTING INFORMATION

Recycling ZnTe, CdTe, and other compound semiconductors via ambipolar electrolysis

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A. EXPERIMENTAL SETUP

Electrodes. The working electrode (WE) comprised a 1.98 mm-diameter glassy carbon (GC) rod (Alfa-Aesar) sheathed by boron nitride (hot-pressed, Saint Gobain). The exposed section of the glassy carbon was a circle with a surface area of 3.07 mm². The WE was polished to obtain a planar electrode with a smooth surface. An unsheathed GC rod (1.98 mm diameter, Alfa-Aesar) served as the counter electrode (CE). Both the WE and CE were connected to current leads by means of a graphite coupler. Each current lead was a 3 mm diameter stainless steel rod, sheathed by an alumina tube, sealed with epoxy, and fed through compression fittings in the vessel cap. For the ZnCl₂ experiments, the reference electrode (RE) was a 3 mm diameter brass rod (McMaster-Carr, 30 wt% Zn, 70 wt% Cu) which established a stable potential between Zn²⁺ in the molten salts and Zn in the brass (Zn_{brass}). Zn_{brass} has less than unit activity, so the electrochemical potential of each RE was determined by measuring the open circuit potential (OCP) between the RE and the WE onto which had been electrodeposited a coating of elemental Zn. This gave the potential difference between the standard potential of Zn|Zn²⁺ and Zn_{brass}|Zn²⁺. The RE was measured as 109 mV more anodic than Zn at 500 °C and varied with temperature. The electrical potential difference between two identically constructed brass REs was < 1 mV and drifted at a rate of < 0.15 mV/hr (Suppl. Figs 3a-b). Electrochemical potentials, E, are

reported versus the standard potential of Zn|Zn²⁺.

Salt handling. Salts were handled in an argon-filled glovebox and electrochemical tests were performed in a sealed stainless steel vessel. The first part of the study consisted of three-electrode electrochemical scans in melts of ZnCl₂ and ZnTe over a range of ZnTe concentrations and temperatures. 300 g of ZnCl₂ salt and 0 g to 6.02 g of ZnTe were used, depending on the desired ZnTe concentrations. The ZnCl₂-ZnTe mixtures were added to a quartz crucible and placed at the bottom of a 55 cm tall stainless steel vessel. The electrodes and quartz crucible containing the salts were assembled within the stainless steel vessel, sealed, removed from the glovebox, and placed inside a vertical tube furnace. The bottom of the vessel was inside the hot zone of the furnace while the top remained outside. The top was water-cooled to allow the use of rubber o-rings which made the system gas tight. The temperature of the salt mixture was measured directly using a type-K thermocouple, sheathed by a close quartz tube. The CdTe experiment was set up in a similar manner, using 327 g of CdCl₂, 133 g of KCl, and 8.6 g of CdTe.

Salt drying. Steps were employed to remove any residual moisture. After sealing the salts inside the test vessel, the salts were held for 12 h at 80 °C under vacuum ((2.7 ± 0.5)_Pa) then heated at a

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rate of 1 °C/min up to 240 °C and held for additional 4 h until the pressure again reached vacuum ((2.7 ± 0.5) Pa). Electrochemical scans were free of peaks associated with residual moisture. After drying, the vessel was backfilled with argon (99.999 %, Airgas), heated to 500 °C, and allowed to equilibrate for 12 h to 60 h before the onset of experiments. This equilibration time was required to fully dissolve ZnTe, as revealed by electrochemical scans (Suppl. Figs. 4a-b).

Electrolysis. Electrolysis was performed on a melt of ZnCl₂ with dissolved ZnTe, producing liquid Zn and liquid Te. Electrolysis cells were identical to the electrochemical setup described above except that the WE and CE were replaced with ‘cup electrodes’ that were able to collect the molten metals for post process analysis. The cup electrodes consisted of a CE placed inside a closed-end mullite tube, such that the GC rod touched the bottom of the closed end of the tube. A hole was cut into the side of the mullite tube 1 cm above the closed end, allowing salt to enter and come in

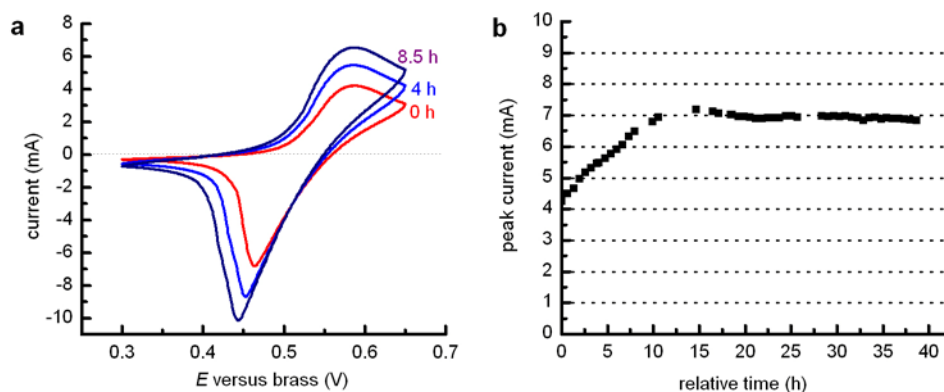
contact with the GC rod. During electrolysis metal deposited onto the GC rod and fell to the bottom of mullite tube where it collected. After removing from the cell, the metal deposit was analyzed and its purity was measured.

Bulk chemical analysis: These analyses were performed by Luvak, Inc. using the following methods: Carbon and sulfur levels were analyzed using a combustion infrared detection – ASTM E 1019-08, oxygen and nitrogen were analyzed using an inert gas fusion – ASTM E 1019-08, hydrogen was detected using inert gas fusion – ASTM E 1447-09, chloride levels were analyzed using an ion selective electrode method – ASTM D 512-04, fluoride levels were analyzed using an ion selective electrode method – ASTM D 1179-04, bromide & iodide levels were analyzed using an ion selective electrode method – ASTM D 1246-10. All other element composition levels were analyzed using direct current plasma (DCP) emission spectroscopy – ASTM E 1097-07.

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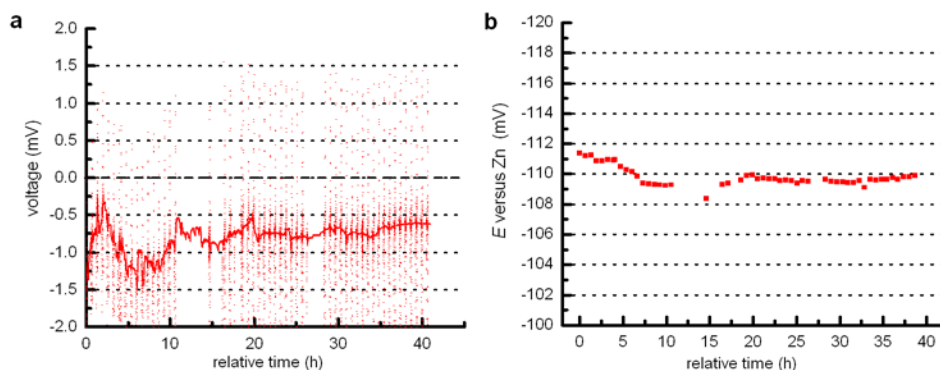
B. FIGURES



Supporting Figure 1. ZnTe dissolution in ZnCl₂ at 500 °C. **a**, Cyclic voltammograms (CV) of a melt containing 0.5 mol% ZnTe at different times after the melt reached 500 °C ($\nu = 10$ mV/s). The peak height increased with time as ZnTe dissolved. The working electrode was an unsheathed glassy carbon rod, 2 mm diameter, immersed approximately 1.5 cm into the melt. **b**, CV peak height evolved as a function of time. After 12 h, the peak height stopped increasing. Since the melt is below the saturation limit of ZnTe, these data indicate that ZnTe is fully dissolved by that time.

SUPPORTING INFORMATION

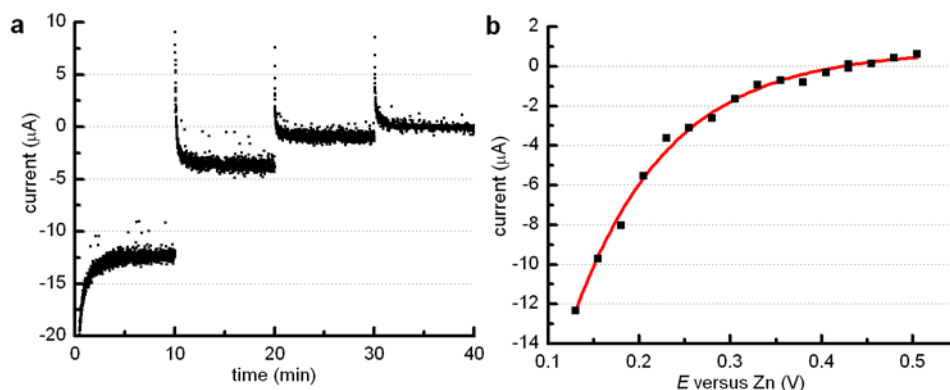
Recycling ZnTe, CdTe, and other compound semiconductors by ambipolar electrolysis



Supporting Figure 2. Brass rod reference electrode calibration in molten ZnCl_2 at $500\text{ }^\circ\text{C}$. **a**, Open circuit potential (OCP) measurements between two identically constructed brass rod reference electrodes (RE). Comprised of 30 wt% Zn and 70 wt% Cu, electrodes established a potential with the ZnCl_2 melt by means of the Zn/Zn^{2+} couple. Spikes in signal were due to electric fields in the melt generated by electrochemical scans performed on separate electrodes. RE potentials deviated by $< 1\text{ mV}$ and the maximum drift rate was $< 0.15\text{ mV/h}$. **b**, OCP difference between a brass RE and the WE onto which a thin layer of Zn had been electrodeposited at $500\text{ }^\circ\text{C}$. A potential difference of -109 mV was measured, owing to the less than unit activity of Zn in the alloy. After 12 h of equilibrating, the RE stability was $\pm 0.5\text{ mV}$. Electrochemical potentials for other scans are provided versus the Zn/Zn^{2+} standard potential and were calibrated during each experiment.

SUPPORTING INFORMATION

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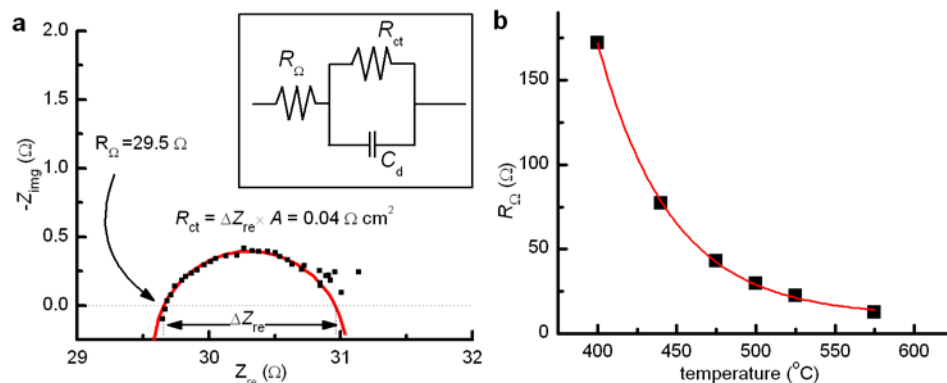


Supporting Figure 3. DC stepped potential for electronic conductivity measurements. **a**, Current response under applied stepped potentials of $E = (0.13, 0.23, 0.33, 0.43)$ V versus Zn. After a transient period the current plateaus at a fixed value. At these potentials, Faradaic processes are inactive, suggesting that current is due to electronic conduction. **b**, Steady state current is plotted as a function of potential, indicating an exponential response, consistent with other work[†]. The slope of the line is a measure of the electronic resistance of the melt, and is in the range of 11,000 Ω to 100,000 Ω . The resistance is dependent on the geometry of the cell and positioning of the electrodes, so measurements from different experiments can not be directly compared.

[†] Liu, J.; Poignet, J. *Journal of Applied Electrochemistry* **1992**, *22*, 1110-1112.

SUPPORTING INFORMATION

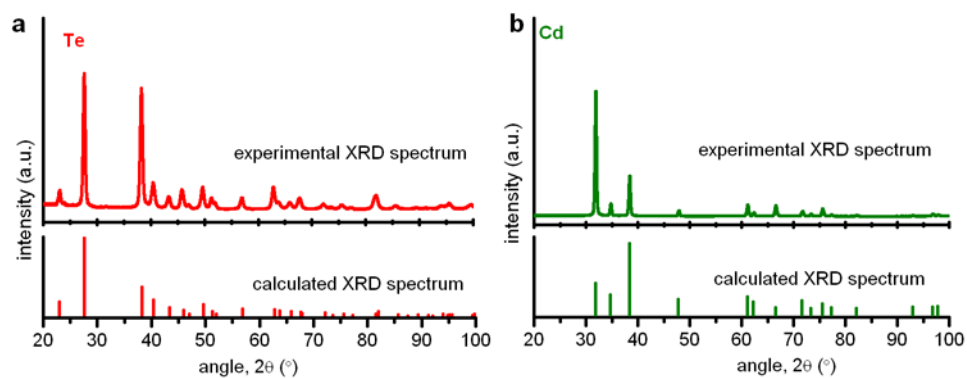
Recycling ZnTe, CdTe, and other compound semiconductors by ambipolar electrolysis



Supporting Figure 4. AC impedance response. **a**, AC impedance spectroscopy for a ZnCl_2 melt with 0.5 mol% ZnTe at 500 $^{\circ}\text{C}$. The equivalent circuit for the $(\text{Zn}^{2+} + 2\text{e}^{-} \leftrightarrow \text{Zn})$ Faradaic reaction is also shown (inset). The solution resistance, R_{Ω} , was a measure of the total electrical conductance (ionic and electronic), and is much lower than the purely electronic conductance (Suppl. Fig. 1a-b), indicating that melt electrical conductance was dominantly ionic. By taking the ratios of the relative conductances, the electronic portion was calculated to be $< 0.3\%$ of the total conductance. The charge transfer resistance, R_{ct} , was determined from these data as shown. Similarly, AC impedance scans for electrodeposited Te did not produce characteristic semi-circles, owing to Te solubility or poor wetting on glassy carbon. **b**, The solution resistance exhibited an exponential decay with temperature.

SUPPORTING INFORMATION

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Supporting Figure 5. Ambipolar electrolysis of CdTe. **a**, Experimental XRD spectrum of metal deposited at the anode (top) and calculated spectrum of Te metal (bottom). Deposit was phase-pure Te. **b**, Experimental XRD Spectrum of metal deposited at the cathode (top) and calculated spectrum of Cd metal (bottom). Deposit was phase-pure Cd.

SUPPORTING INFORMATION

Recycling ZnTe, CdTe, and other compound semiconductors by ambipolar electrolysis

C. TABLES

a) ZnTe electrolysis products

Element	Zn sample (wt %)	Te sample (wt %)
Copper	0.0280	0.1600
Nickel	0.0014	0.0069
Cadmium	0.0005	< 0.0005
Chromium	< 0.0005	0.0014
Iron	1.8400	0.0009
Sodium	< 0.0005	0.0009
Calcium	< 0.0005	0.0006
Silicon	< 0.0010	0.0043
Zinc	Alloy	0.1100
Tellurium	0.0490	Alloy
Chloride	< 0.0010	< 0.0010
Fluoride	< 0.0010	0.0570
Bromide	< 0.0010	< 0.0010
Iodide	< 0.0010	< 0.0010
Nitrogen	0.0017	< 0.0010
Oxygen	0.0300	0.0064
Carbon	0.0098	-- ²
Sulfur	< 0.0010	-- ²
Hydrogen	0.0038	-- ²

--² Limited sample, sample consumed

b) CdTe electrolysis products

Element	Cd sample (wt %)	Te sample (wt %)
Copper	0.0170	0.0019
Nickel	0.0480	0.0560
Cadmium	Alloy	0.7800
Chromium	< 0.0005	< 0.0005
Iron	0.0005	0.0005
Sodium	<0.0005	< 0.0005
Calcium	<0.0005	< 0.0005
Silicon	<0.0010	< 0.0010
Zinc	<0.0005	< 0.0005
Tellurium	< 0.0020	Alloy
Chloride	< 0.0010	< 0.0010
Fluoride	0.0022	0.0024
Bromide	< 0.0010	< 0.0010
Iodide	< 0.0010	< 0.0010
Nitrogen	< 0.0010	-- ²
Oxygen	0.0035	-- ²
Carbon	0.0030	-- ²
Sulfur	< 0.0010	-- ²
Hydrogen	0.0003	-- ²

--² Limited sample, sample consumed

Supporting Table 1 | Bulk compositional analysis. a, Results from Zn and Te samples from ZnTe electrolysis. **b,** Compositional results from Cd and Te products from CdTe electrolysis.