

## Thermoelectrochemical Cell with Molten Carbonate Electrolyte

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### Abstract

Industrial processes for production of metals and alloys by metallurgical and electrochemical methods generate a lot of heat due to irreversible losses. The waste heat should be used to generate electricity. Commercial thermoelectric generators based on semiconductor materials have limited power efficiency. Alternative thermoelectric cells using molten salt electrolytes and symmetrical gas electrodes may be developed for power production without the use of expensive and critical materials. Experiments were carried out in the molten  $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$  system at different compositions at temperatures from 550 - 850°C. Effects of adding  $\text{CaCO}_3$  were also studied. Reversible electrodes with respect to carbonate ions were established by using gas mixtures of  $\text{O}_2$  and  $\text{CO}_2$ . Solid  $\text{MgO}$  particles were added to the molten electrolyte in order to improve the conditions for thermoelectric conversion. Two identical electrodes of gold were located at different temperatures for determining the Seebeck coefficient based on potential measurements. Seebeck coefficients up to ~1.5 mV/K were obtained. The possibility to combine a thermoelectrochemical cell and a battery or a fuel cell in a hybrid electrochemical power generating system is an interesting option which will be explored.

### Introduction

Primary production of metals is a major industry world wide, spending huge amounts of energy and emitting large quantities of  $\text{CO}_2$  gas. These metallurgical and electrochemical processes operate at high temperatures and produce lots of waste heat due to irreversible losses. There is a big potential for utilising waste heat, and the use of thermoelectric generators is a possibility.

A thermoelectric generator converts heat into electricity through the Seebeck effect [1]. Commercial thermoelectric generators are based on solid semiconductor materials. Electricity can be generated by placing thermoelectric materials at different temperatures.

An alternative thermocell can be developed by using an ion conducting electrolyte such as a molten salt combined with symmetrical gas electrodes. The two electrodes are placed at different temperatures, and a potential is developed due to the transport of ions in

the electrolyte. The ability to generate electricity depends on the Seebeck coefficient of the cell which is given by the gradient of the reversible potential and the temperature difference:

$$\alpha_s = \frac{\Delta E^{rev}}{\Delta T} \quad (1)$$

where  $\alpha_s$  is the Seebeck coefficient.

The efficiency of the thermocell also depends on the heat conductivity and the electrical conductivity and may be expressed by the so-called figure of merit:

$$ZT = \frac{\alpha_s^2}{\lambda R} T \quad (2)$$

where  $\lambda$  is the heat conductivity and  $R$  is the electric resistance of the electrolyte.

The Seebeck coefficient is made up of the various entropy contributions from the electrodes, electrode surfaces and the electrolyte. The following equation which is valid at steady state conditions was derived in a previous paper [2]:

$$\alpha_s = -\frac{1}{F} \left( \frac{1}{2} S_{CO_2} + \frac{1}{4} S_{O_2} - \frac{1}{2} S_{CO_3^{2-}}^* \right) \quad (3)$$

where  $S_j$  is the entropy of component  $j$  at average temperature of the electrodes  $T$  and pressure  $p_j$ . The term  $S_{CO_3^{2-}}^*$  is the transported entropy of the carbonate ion. The entropies and the transported entropies are generally functions of temperature.

The aim of this project is to generate electricity from waste heat in metal producing industries by developing thermoelectric generators based on symmetrical electrochemical cells with molten salt electrolytes. The advantages of the proposed idea are high Seebeck coefficients and no use of expensive, poisonous or critical materials.

In the present work solid particles of MgO are dispersed in the electrolyte in order to improve the thermoelectric properties of the cell. This approach was first suggested by Jacobsen and Broers [4]. MgO has a very low solubility in the molten carbonate electrolyte. The presence of a solid phase may reduce the heat conductivity of the electrolyte and make for a more stable reading of the potential. A gas mixture of CO<sub>2</sub>/O<sub>2</sub> is used to obtain electrodes reversible to the carbonate ion.

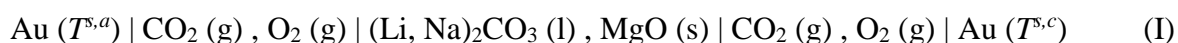
## Experimental

Lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), calcium carbonate (CaCO<sub>3</sub>) and magnesium oxide (MgO) were from Sigma-Aldrich with purity > 99 %. Pre-made electrode gas mixtures containing 34% oxygen mixed with carbon dioxide were from AGA, Norway. Gold sheet and wire for the electrodes and wires of platinum, platinum with 10% Rhodium for thermocouple fabrication were from K.A. Rasmussen, Norway. Alumina tubes with one center bore 2.3 mm diameter and four other bores with 0.75 mm diameter and a tubular crucible were from MTC Haldenwanger, Germany. The flow rate of electrode gas supplied through the ceramic tubes was controlled

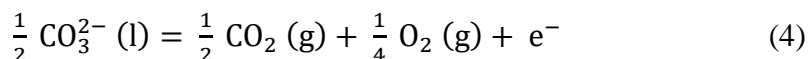
by a pair of Brooks instrument Sho-Rate flow meters with  $\pm 5\%$  accuracy. The temperature of the electrodes and the cell potential were recorded by Agilent, 34972A data acquisition unit.

The thermo-electrochemical cell was constructed in a standard laboratory vertical tubular furnace and shown in Figure 1. The cell consisted of a sintered tubular crucible, with two electrodes immersed in the molten carbonate electrolyte. In each alumina tube, the gold wire was inserted into the center bore (2.3 mm diameter) of a 5-bore  $\text{Al}_2\text{O}_3$  tube and the gold sheet was point-welded to the wire. The thermocouple (Pt-Pt10%Rh) was inserted into two of the other holes (diameter 0.75 mm) and the junction was positioned as near as possible to the gold sheet.  $\text{CO}_2/\text{O}_2$  gas was supplied through the bores of the ceramic tube.

The electrochemical cell with gas electrodes, reversible to the carbonate ion, held at different temperatures can be represented as:



The electrode reaction is:



A temperature difference ( $\Delta T$ ) was established between the electrodes by positioning them at different heights in the crucible. The temperature difference was always smaller than  $20^\circ\text{C}$ . The reversible cell potential was measured as a function of the temperature difference, after an equilibration period of 10-20 min. The electrolyte preparation and cell measurements were performed using the same procedure as in our previous publications [2, 3].

## Results and discussion

The steady state cell potential at zero current was recorded as a function of the temperature difference between the electrodes as shown in Figure 2a, where the time variation is also shown. The results in Figure 2a were obtained in the ternary electrolyte mixture of  $(\text{Li}, \text{Na}, \text{K})_2\text{CO}_3$  at  $430^\circ\text{C}$ . The recorded reversible potentials were plotted against the temperature difference as shown in Figure 2b. The Seebeck coefficient was determined from the slope of the linear fit. The Seebeck coefficients were found to be similar to previously reported values [2, 3]. The obtained results are given in Figure 3. The value of the Seebeck coefficient was found to vary from 0.9 mV/K in ternary  $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{+MgO}$  at  $405^\circ\text{C}$  to 1.7 mV/K in binary  $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$  at  $550^\circ\text{C}$ . Additions of  $\text{CaCO}_3$  gave lower values.

By optimising the flow rate of the mixed gas to be  $\sim 20$  mL/min it was observed that the steady state condition was achieved after very short times as shown in Figure 2b. At low and high flow rates it took longer to reach steady state, which may be due to problems of achieving a good contact between the three phases of gas, solid and liquid.

Also the content of dispersed MgO was varied. The Seebeck coefficient was unaffected in the range from 44 - 66 vol% MgO. The present results were obtained by using 55 vol% MgO.

By using eq. (3) it is possible to estimate the transported entropy of the carbonate ion. Values ranging from 150 - 200 J/K·mol were obtained.

The measured Seebeck coefficients in molten carbonate electrolytes are much higher than Seebeck coefficients for commercial thermoelectric cells probably due to the use of reversible gas electrodes [4 - 6]. The figure of merit was estimated to be 0.34 for pure molten  $\text{Li}_2\text{CO}_3$  at  $750^\circ\text{C}$  by using eq. (2). These results are promising for the prospect of developing a thermoelectrochemical generator and possibly combined with a molten carbonate fuel cell.

## Conclusions

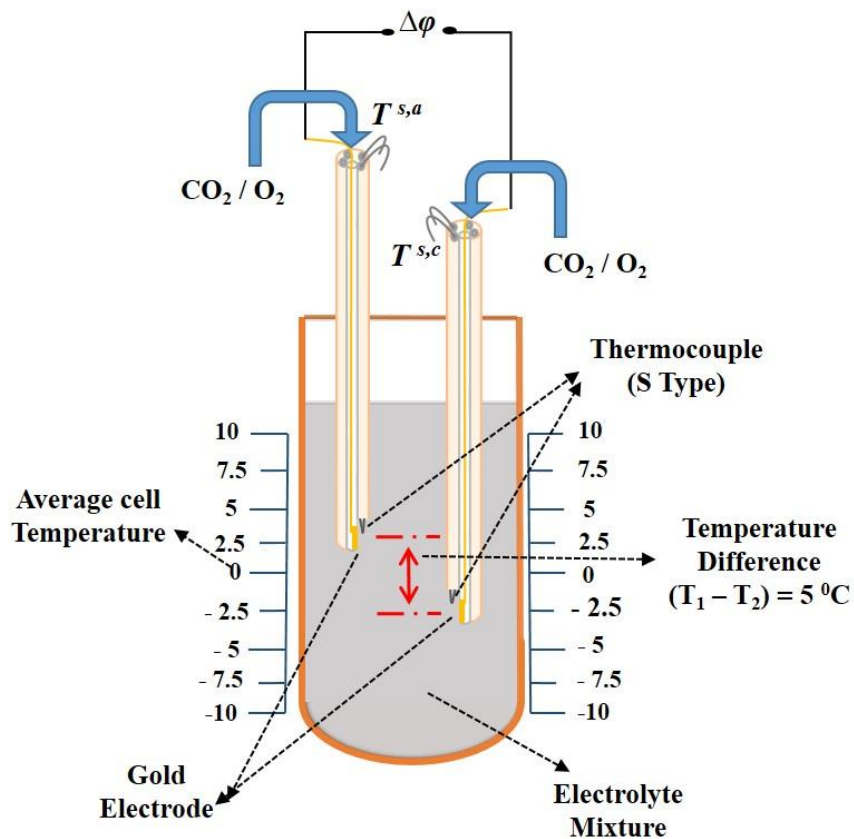
The thermoelectric potential for a molten carbonate thermocell was measured with different flow rates of electrode gas and solid oxide ratios in the electrolyte. Seebeck coefficients up to 1.7 mV/K were obtained. The highest values were obtained in the molten binary mixture  $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ . The rate of the gas flow of  $\text{CO}_2$  and  $\text{O}_2$  was found to influence the Seebeck coefficient. Additions of  $\text{CaCO}_3$  did not improve the Seebeck coefficient.

## Acknowledgements

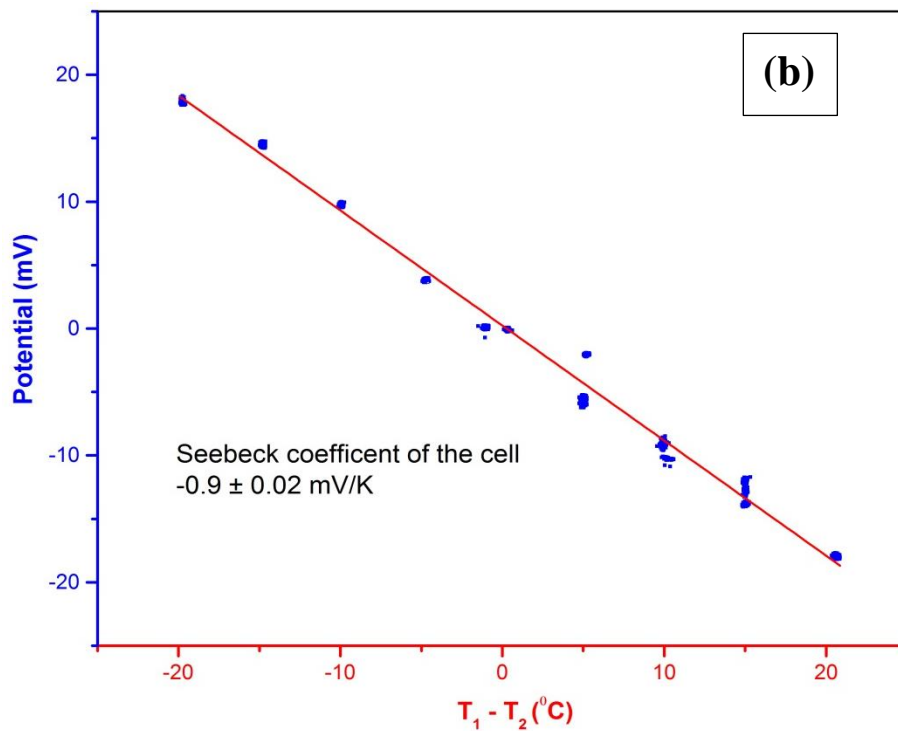
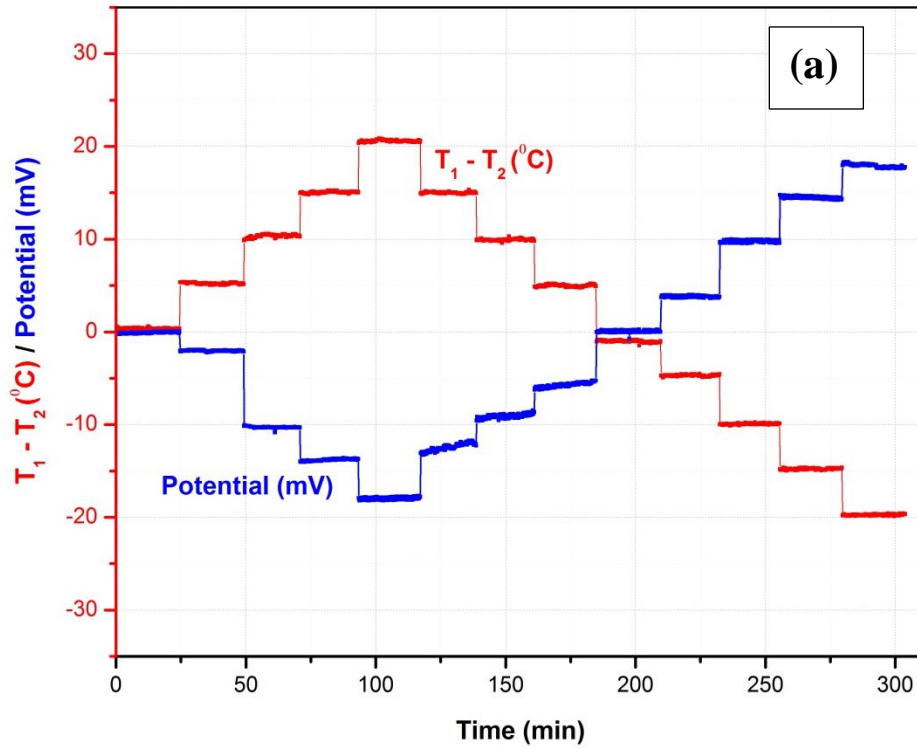
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## References

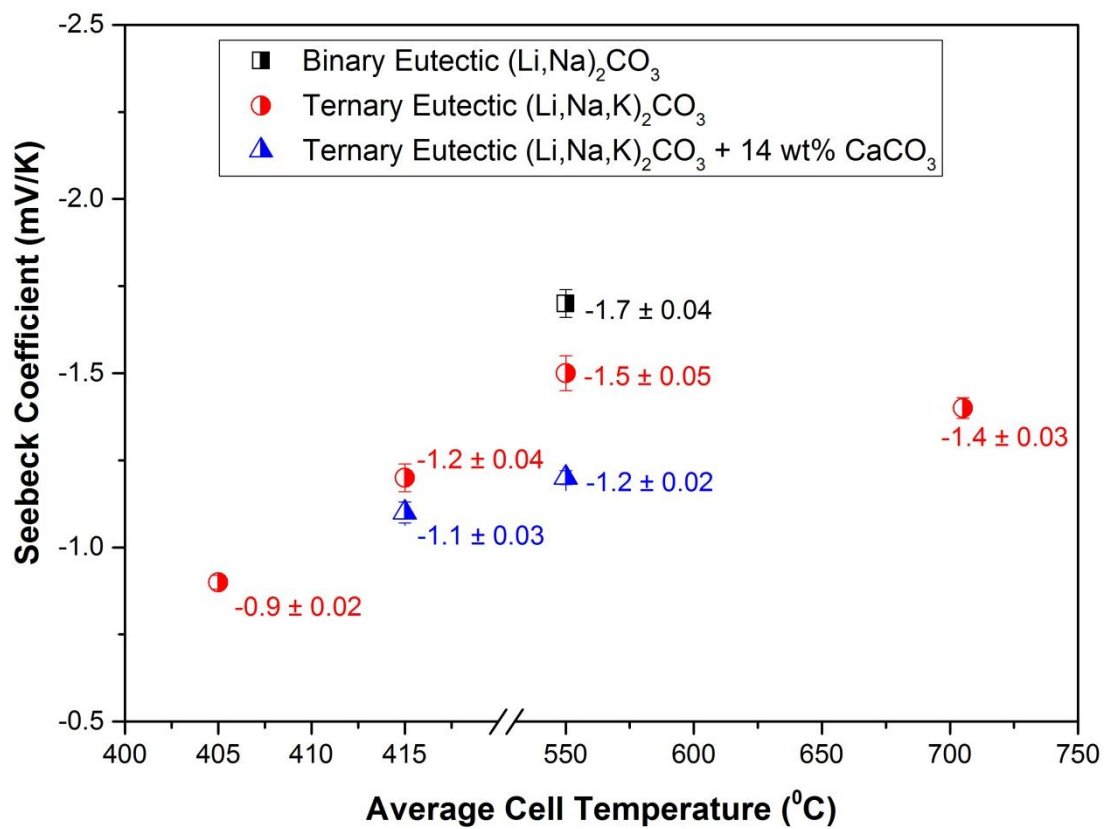
1. E. Bouty, *J. Phys. Theor. Appl*, **9**, 229 (1880).
2. Kang, M. T. Børset, O. S. Burheim, G. M. Haarberg, Q. Xu, and S. Kjelstrup, *Electrochim. Acta*, **182**, 342 (2015).
3. M. T. Børset, X. Kang, O. S. Burheim, G. M. Haarberg, Q. Xu, and S. Kjelstrup, *Electrochim. Acta*, **182**, 699 (2015).
- 4 T. Jacobsen and G. H. J. Broers, *J. Electrochem. Soc.*, **124**, 207 (1977).
5. K. Cornwell, *J. Phys. D. Appl. Phys.*, **1**, 173 (1968).
6. B. Burrows, *J. Electrochem. Soc.*, **123**, 154 (1976).



**Figure 1** Schematic representation of the thermocell (cross-sectional view) used in this study. Electrodes were positioned to establish a temperature gradient between the electrodes, while the cell was maintained at the average cell temperature.



**Figure 2** Thermocell with ternary eutectic molten carbonates melt  $(\text{Li,Na,K})_2\text{CO}_3$  at an average cell temperature of  $405$   $^{\circ}\text{C}$ . **(a)** Change in potential in response to the temperature gradient between the electrodes was plotted against the time scale. **(b)** The plot for Seebeck coefficient calculation.



**Figure 3** Comparison of the Seebeck coefficient obtained for the thermocells with the different cationic composition of the melt in the electrolyte mixture with 55 vol % MgO.