High temperature electrochemical pathways towards low-carbon steelmaking and efficient CO₂ utilization

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Modern steel-making and electric power industries are mainly based on the chemical reactions between carbon (coal) and oxygen (denoted reactions 1-3), which produce tremendous amount of anthropogenic greenhouse gas (GHS) emissions as well as consume huge amount of fossil fuels. It can be estimated from its annual steel and electricity production and coal consumption that more than 4 billion tons of CO₂ emission from steel companies and coal fired power plants in 2012 in China.

\[ C + O_2(g) = CO_2(g) + Q \] (1)
\[ C + CO_2(g) = 2CO(g) + Q \] (2)
\[ FeO_3 + 3 CO = 2 Fe + 3 CO_2(g) + Q \] (3)

The increasing concern of serious change of the global environment with continuously increasing of atmospheric CO₂ concentration has drawn intensive attention on developing renewable energies and low-carbon technologies. Undoubtedly, electricity is the most available form of renewable energies and therefore novel electrochemical technologies would be a very competitive alternative to a low-carbon steel-making (using electron as reductant to replace carbon) and to transform CO₂ back into carbon and oxygen (reverse the reaction (1)).

Efforts of electrolytic production of iron and electrochemical reduction of CO₂ at room temperature have been made in recent years in parallel with high temperature electrolysis. Generally speaking, high temperature molten salt electrolysis has some intrinsic advantages in the view of thermodynamic and kinetic. For example, the theoretic decomposition voltage of Fe₂O₃ into Fe and O₂ at 50°C, 750°C and 1550°C is 1.27V, 0.96V, 0.60V, respectively. The rapid reaction kinetics at high temperature can reduce the over-potential of the electrode reactions so that the overall cell voltage could be much lower than that of room temperature electrolysis cell. On the other hand, rapid reaction kinetics means high space-time yield at high temperature. However, one of the big challenges for a “green” high temperature electrolysis process is seeking a satisfactory non-consumable anode for oxygen evolution. Herein, three kinds of novel high temperature molten salt electrolysis technologies armed with inert anodes for producing eco-iron and utilization of CO₂ investigated by the author and co-workers in recent years, are briefly introduced.

Molten oxide electrolysis (MOE), advocated by Sadoway as a carbon-free alternative to existing metals extraction technology, is the electrolytic decomposition of a molten metal oxide into metal and oxygen gas. Due to the low vapor pressure of oxide melt and its strong adsorption to oxide/ore, the metals with high melting point including Fe, Ti can be produced in liquid state at the temperatures beyond their melting points by MOE. While its success hinges upon the existence of an inert anode sustainably working at the white-heat temperature. An electrolysis cell fitted with an iridium anode in an electrolyte of molten MgO–CaO–SiO₂–Al₂O₃ with iron oxide for producing liquid iron and oxygen gas was realized for the first time. The cell can be operated at a current density above 0.55 A cm⁻². The iridium stability mechanisms can be attributed to the electrochemical formation and simultaneous thermal decomposition of a surface film of iridium oxide. While iridium is too costly and its natural abundance in the earth’s crust is too low to meet the needs of the world steel industry, more recently, a FeCr alloy inert anode for MOE was initially demonstrated by Allanore, Yin and Sadoway.

Electrochemically splitting solid Fe₂O₃ into solid iron and oxygen gas in molten Na₂CO₃–K₂CO₃ at 750°C is an effective alternative way to produce “green” iron. Ni10Cu1Fe alloy was demonstrated a satisfactory inert anode in the melt. The cathodic current efficiency was as high as 95% and the energy consumption for producing 1 kg iron was only 2.87 kWh, oxygen gas was produced on the anode. The stability of Ni10Cu1Fe alloy is due to the formation of a protective and electronic conductive mixed oxide layer on the alloy surface. The reduction of solid Fe₂O₃ involves three steps, with the formation of intermediate products, viz., NaFeO₂ and NaFe₂O₄. The carbon content in iron product was found to be in the range of 0.035–0.76 wt.%, depending on the applied cathodic potential.

A eutectic mixture of Li–Na–K carbonates with certain amount of Li₂O can effectively absorb CO₂ and provide enough wide potential window for CO₂ and carbonate reduction. SnO₂ rod was demonstrated as a successful inert anode for the capture and electrochemical conversion of CO₂ into carbon and oxygen gas in the melt in the temperature range of 400-650 °C. Amorphous carbon was obtained on the cathode with different surface areas of 400-800 m² g⁻¹ and can be applied in a variety of fields such as energy storage and pollutant adsorption. The current efficiency was over 90% and the current density can be as high as 100 mA cm⁻².

It is expected that these novel high temperature electrolysis processes and as such, driven by the renewable energy sources such as solar power, can enlighten a low-carbon future of the global.

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