



Supporting Information

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Sungas Instead of Syngas: Efficient Coproduction of CO and H₂ with a Single Beam of Sunlight

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Syngas is commonly produced to convert solid or gas-phase fossil fuels into liquid fuels.^[2] The conventional steam reformation production of syngas from methane is realized by steam reforming reactions to CO + H₂, given by eqs 1-3:

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and the production of syngas from coal is realized by:



The water shift reaction is then used if more hydrogen is desired from the coal gas product:



The syngas is then used as a feedstock to form methanol, or for Fischer-Tropsch type reactions to produce middle-distillate range fuels of C₁₁-C₁₈ hydrocarbons including synthetic jet, kerosene and diesel fuels.^[3]

Low temperature enhances electrolytic H₂ formation in molten hydroxides. The coulombic efficiency of electrolytic water splitting, η_{H_2} , (moles H₂ generated per 2 Faraday of applied charge) approaches 100% in low melting point, mixed alkali molten hydroxides at temperatures up to 300°C.



Hydroxide hydrates, $\text{MOH}\cdot n\text{H}_2\text{O}$ (M=alkali), bind fewer waters, n, at higher temperature, equilibria, and saturated aqueous alkali hydroxide solutions contain less water. For example, saturated NaOH solution equilibrate with 23%, 16% or 3% water respectively at 100°C, 200°C or 300°C (saturated aqueous NaOH solution do not boil at 1 atmosphere of pressure^[3]), As temperature increases, molten alkali hydroxides provide a decreasing source of water for hydrogen generation as they lose water favoring the formation of the oxide:



For example, as temperature increases by 100°C increments from 500°C to 900°C, the equilibria constant for the LiOH reaction of eq 5 (M=Li), increases from 0.006, 0.02, 0.1, 0.3, to 0.8.^[23] At higher temperature the coulombic efficiency of hydrogen generation in molten hydroxide falls as superoxide, O_2^- reduction, increasingly competes with hydrogen formation in the (parasitic) side reactions:^[19]

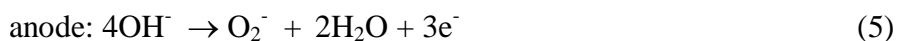


Table S1. The measured coulombic efficiency of hydrogen generation, η_{H_2} , in various molten hydroxide electrolytes at various temperatures. Water (as steam) is bubbled through the electrolyte. Electrolytic water splitting is measured at 267 mA cm⁻² (1 A) between two planar 3.75 cm² nickel electrodes. Efficiency is determined by comparing the measured mole equivalents of hydrogen generated to each 2 mole equivalents (coloumbs) of applied current in accord with $\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2\text{O}_2$.

Electrolyte	Melting Point	$\eta_{\text{H}_2}(200^\circ\text{C})$	$\eta_{\text{H}_2}(300^\circ\text{C})$	$\eta_{\text{H}_2}(400^\circ\text{C})$	$\eta_{\text{H}_2}(500^\circ\text{C})$	$\eta_{\text{H}_2}(600^\circ\text{C})$	$\eta_{\text{H}_2}(700^\circ\text{C})$	$\eta_{\text{H}_2}(800^\circ\text{C})$
LiOH	462°C				88%	21%	4%	0%
Li _{0.3} Na _{0.7} OH	215°C		99%	87%	47%			
NaOH	318°C			72%				
Na _{0.5} K _{0.5} OH	170°C	96%	86%	47%	28%	13.4%		
KOH	406°C			80%				
Li _{0.3} K _{0.7} OH	225°C		94%	56%	32%	7.8%		
Ba(OH) ₂	407°C				55%	32%		
Li _{0.33} Ba _{0.67} (OH) ₂			96%					
(NaOH) _{0.865} (Na ₂ CO ₃) _{0.125}				77%				
(LiOH) _{0.843} (Li ₂ CO ₃) _{0.157}					79%	17.2%	5.5%	

