Electronic Supplementary Material (ESI) for RSC Advances.
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Supporting Information

1. Potential difference of the H^+/H_2 and Ni^{2+}/Ni electrode evaluated by thermodynamic calculation.

The standard potential difference between H^+/H_2 and Ni^{2+}/Ni at 400-800℃ was calculated by the standard free energy ΔG of the following two cell reactions:

$$NiF_2 + H_2(g) = Ni + 2HF(g) \quad (1)$$

$$NiCl_2 + H_2(g) = Ni + 2HCl(g) \quad (2)$$

Where the $\Delta G = nF\Delta E$, ΔE is the standard potential difference between H^+/H_2 and Ni^{2+}/Ni, n is the number of the transferred electron, F is the Faraday constant. The calculated ΔE were list in the following Table S1.

Table S1 The standard potential difference between H^+/H_2 and Ni^{2+}/Ni at 400-800℃

Temperature (℃)	ΔG of eq (1) (KJ mol^{-1})	ΔG of eq (2) (KJ mol^{-1})	ΔE in fluoride system (V)	ΔE in chloride system (V)
400	-4.037	5.754	-0.021	0.030
450	-12.287	-2.298	-0.064	-0.012
500	-20.485	-10.285	-0.106	-0.053
550	-28.632	-18.209	-0.148	-0.094
600	-36.728	-26.075	-0.190	-0.135
650	-44.776	-33.886	-0.232	-0.176
700	-52.777	-41.645	-0.273	-0.216
750	-60.732	-49.355	-0.315	-0.256
800	-68.642	-57.019	-0.356	-0.295

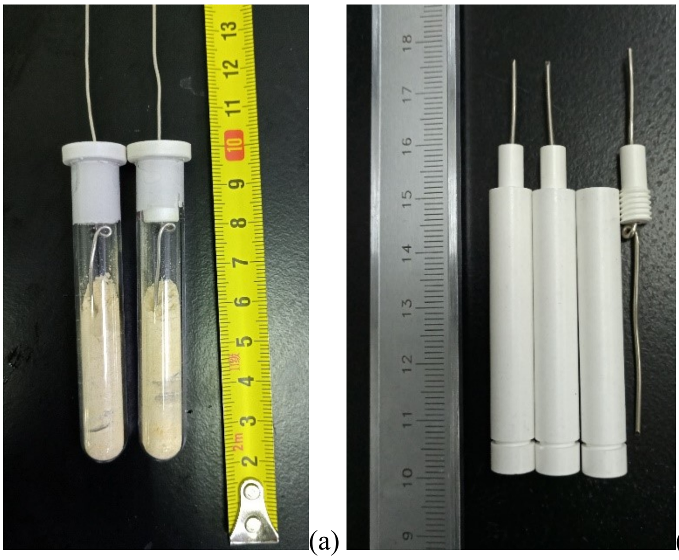
2. The H^+/H_2, Ni electrode employed in this study.

The photo of the H^+/H_2, Ni was shown in Fig. 1S. The H^+/H_2, Ni electrode was made from a nickel pipe (φ6*3.5) and a nickel foil belt (width 8mm thickness 0.05mm) which were bound together by a nickel wire (φ1mm). The apparent working area of the H^+/H_2, Ni electrode was evaluated by the total surface of the nickel material that immersed into the molten salts.

Fig. 1S The photo of the H^+/H_2, Ni made from nickel pipe and nickel foil employed in this study

3. The Ni^{2+}/Ni reference electrodes employed in this work.

A $NiCl_2/Ni$ reference electrode (Fig.2S(a) 20wt% $NiCl_2$ mixed with 80wt% MNKC salts and sealed in a Pyrex glass tube) and a NiF_2/Ni reference electrode (Fig.2S(b) 20wt% NiF_2 mixed with 80wt% FLiNaK salts and sealed in a Hot-pressed Boron Nitride (HBN) tube) was employed for the electrochemical investigation of H^+/H_2, Ni electrode in MNKC and FLiNaK melts, respectively. The potential shift of the $NiCl_2/Ni$ and NiF_2/Ni reference electrode in MNKC or FLiNaK melts is about -7 and -5 mV/h at 600℃, respectively. To avoid the importing of trace oxygen from Pyrex or HBN into the purified molten salts, a 99.95% Pt wire (φ1mm) was used as pseudo reference electrode in both chloride and fluoride molten salt system for voltammetry studies.



(a) (b)

Fig. 2S The photos of the Ni^{2+}/Ni reference electrode. (a) $NiCl_2/Ni$ reference electrode used in MNKC melts, 20wt% $NiCl_2$-80wt% MNKC filled in a Pyrex glass tube. (b) NiF_2/Ni reference electrode used in FLiNaK melts, 20wt% NiF_2-80wt% FLiNaK filled in a HBN tube.

4. The stability of the polarization potential of the H^+/H_2, Ni electrode under a consistent current.

A consistent current electrolysis was performed between the H^+/H_2, Ni electrode and the nickel vessel (counter electrode) for 4h. The potential of the H^+/H_2, Ni electrode was recorded vs the $NiCl_2/Ni$ reference electrode. Results in Fig.3S indicated that the polarization potential of the H^+/H_2, Ni electrode under a 20mA consistent current kept at a relative stable level upon the consideration of the potential shift of the $NiCl_2/Ni$ reference electrode.

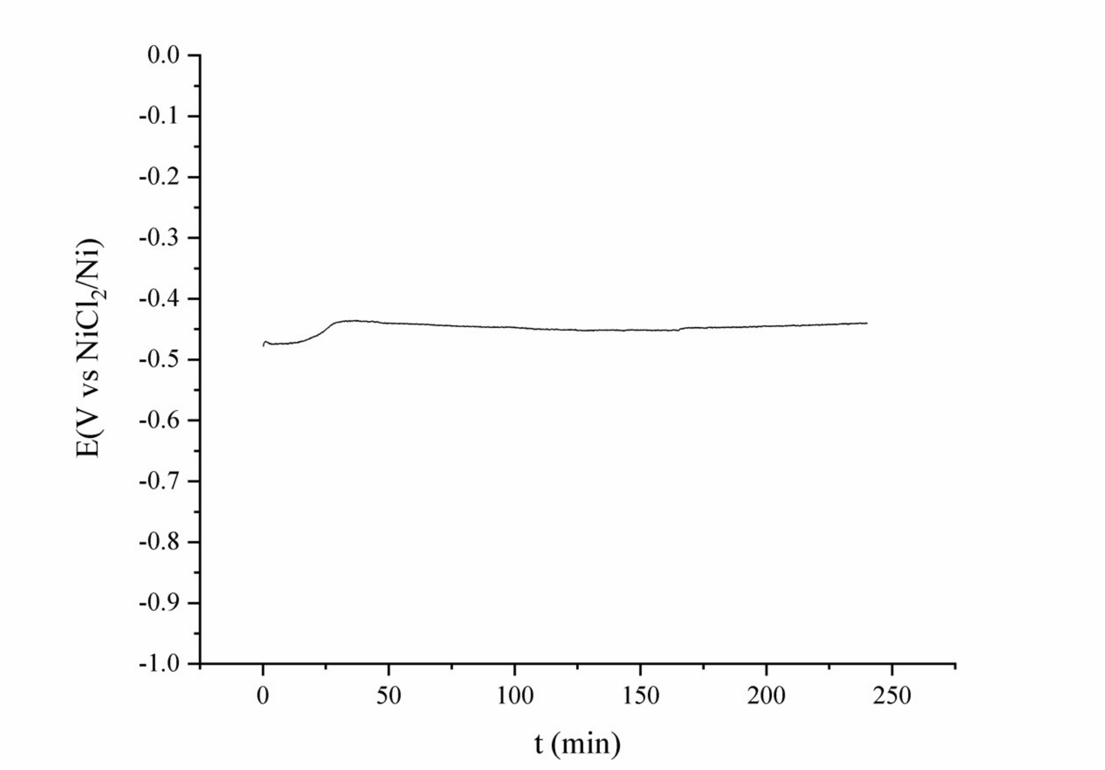


Fig. 3S Potential variation of the H^+/H_2, Ni electrode in a consistent current electrolysis in the MNKC melts at 600℃. H_2 flow rate 150 cm^3/min. Current 20 mA.

5. Thermodynamic evaluation for the stability of $CrCl_2$ or $CrCl_3$ with H_2 at 400-800℃.

The thermodynamic calculations of the reaction of H_2 with $CrCl_2$ or $CrCl_3$ at 400-800℃ was performed and the plots of ΔG vs temperatures were given in Fig. 3S. Results indicated that the Cr^{3+} could be reduced to Cr^{2+} by H_2 gas at 500-800℃. While the Cr^{2+} will be stable in the molten salts with the existence of H_2 at the experimental temperature range.

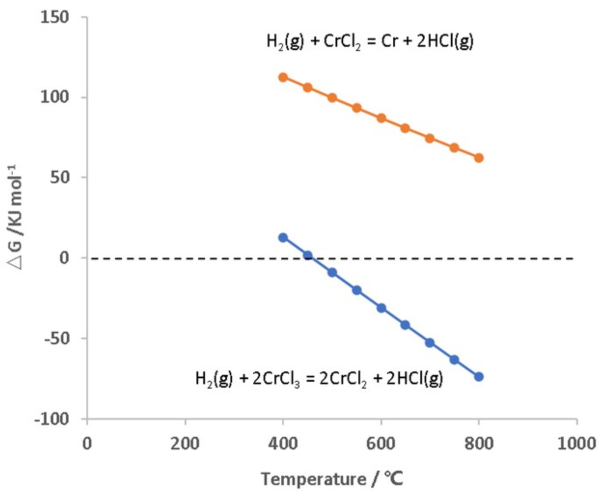


Fig. 4S The thermodynamic calculations of the reaction of H_2 with $CrCl_2$ or $CrCl_3$ at 400-800℃