Valence and Coordination Form Transition of Tungsten Ions in Molten Alkali Chlorides

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Calibration of Ag/AgCl reference electrode potential:

The Ag/AgCl reference electrode was prepared by inserting a Ag wire with a diameter of 1.0 mm in a mullite tube contained 0.1 mol% silver chloride solution in the molten LiCl, LiCl–KCl, NaCl–KCl, NaCl–CsCl and KCl–CsCl, respectively. Pt wire was used as the working electrode and graphite as the counter electrode. The calibration of Ag/AgCl reference electrode potential was carried out by using galvanic square wave technology.

At a constant current of 0.5 A, electrolysis was carried out for 5 s to produce Cl_2 in the molten salt system. Then powered off for 5 seconds and did it three times in this way to calibrate the potential of the reference electrode. Figure 1s showed the potential variation of the Pt electrode versus the Ag/AgCl reference electrode during the electrolysis in NaCl–KCl. The potential of the Pt electrode at the first point after turning off the current represented the potential of Cl_2/Cl^- without over potential of Cl_2 generation. Compared with Ag/AgCl electrode, the average value of E_{Cl2/Cl^-} after three repetitions was about 1.3573 V. Therefore, the electrode potential of Ag/AgCl reference electrode in NaCl–KCl was calibrated to –1.3573 V vs E_{Cl2/Cl^-}. Molten LiCl, LiCl–KCl, NaCl–CsCl and KCl–CsCl were also calibrated in the same way. Table 1s listed the relationship between potential and Cl_2/Cl^- in various molten salt systems.

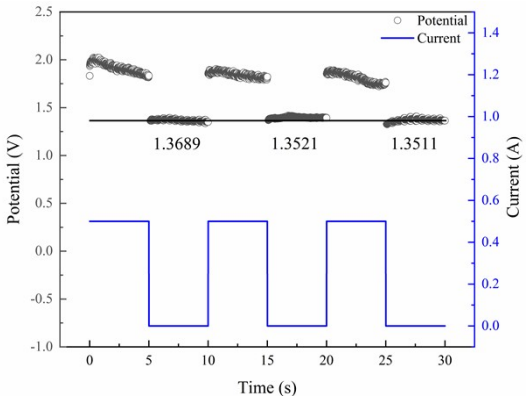

Figure 1s. Calibration of Ag/AgCl reference electrode in NaCl–KCl molten salt system at 1023 K.

Table 1s. The average potential of Ag/AgCl reference electrode versus Cl_2/Cl^- in various molten salt system at 1023 K.

Molten salt	LiCl	LiCl–KCl	NaCl–KCl	NaCl–CsCl	KCl–CsCl
Potential, *E* / V	–1.2951	–1.3278	–1.3573	–1.3677	–1.3702