Efficient electrosynthesis of silver(II) salts

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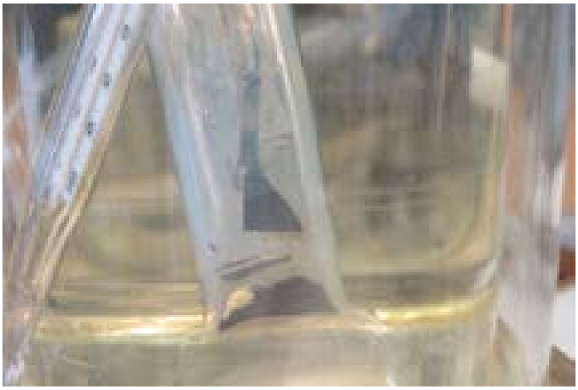
The standard redox potential of the Ag(II)/Ag(I) redox pair reaches some 2 V vs. NHE, which renders Ag(I) notoriously difficult to oxidize in aqueous environment due to preceding oxidation of water. However, Ag(II) species may easily be obtained in non-aqueous media, and in some they may be sufficiently short-lived to enable preparation of genuine Ag(II) salts. Here we will discuss our recent attempts to understand electrochemistry of Ag(II) in anhydrous H_2SO_4 [1,2] and HF [3]. It turns out that oxidation of Ag(I) in H_2SO_4 leads to $[Ag(II)(HSO_4)_2(H_2SO_4)_2]$ complex partly soluble in the solvent; the formal redox potential in 30% oleum reaches +2.9 V vs. NHE, which is the largest experimentally determined value for fluorine-free system [4]. Upon prolonged electrolysis black residue of $Ag(II)(SO_4)$ semiconductor [1] precipitates from the solution.

Similar experiments carried out in anhydrous HF lead to formation of AgF_2. This compound is currently considered to be the only known analogue of parent compounds of oxocuprate superconductors [5] and intense research is carried out worldwide in attempts to dope this system. Success of preparative elecrosynthesis of AgF_2 opens new route towards doped and mixed-valence systems which are of immense important for solid state physics. Further efforts in this direction might lead to expansion of the family of the Ag(II)/F systems known to date [6].



Recent Publications

1. Połczyński P, Gilewski TE, Gawraczyński J, Derzsi M, Gadomski W, Leszczyński PJ, Mazej Z, Jurczakowski R, Grochala W (2016) Efficient electrosynthesis of Ag(II)SO4, powerful oxidizer and narrow band gap semiconductor. European Journal of Inorganic Chemistry (35): 5401–5404.
2. Połczyński P, Jurczakowski R, Grochala W (2013) Strong and long-lived free-radical oxidizer based on silver(II). Mechanism of Ag(I) electrooxidation in concentrated H2SO4. Journal of Physical Chemistry C

117(40): 20689-20696.

3. Połczyński P, Jurczakowski R, Grzelak A, Goreshnik E, Mazej Z, Grochala W (2019) Preparative electrosynthesis of strong oxidizers at boron doped diamond electrode in anhydrous HF. Submitted, for Chemistry, a European Journal.
4. Połczyński P, Jurczakowski R, Grochala W (2013) Stabilization and strong oxidizing properties of Ag(II) in a fluorine-free solvent. Chemical Communications 49(68): 7480-7482.
5. Gawraczyński J, Kurzydłowski D, Ewings R, Bandaru S, Gadomski W, Mazej Z, Ruani G, Bergenti I, Jaroń T, Ozarowski A, Hill S, Leszczyński PJ, Tokár K, Derzsi M, Barone P, Wohlfeld K, Lorenzana J, Grochala W (2019) The silver route to cuprate analogs. Proceedings of the National Academy of Sciences of the USA in press.
6. Grochala W, Hoffmann R (2001) Real and Hypothetical Intermediate-Valence Fluoride AgII/AgIII and AgII/AgI Systems as Potential Superconductors. Angewandte Chemie International Edition in English 40 (15): 2742-2781.

Biography

Wojciech Grochala (b.1972) studied chemistry at the University of Warsaw (Poland) and received his PhD in molecular spectroscopy under the supervision of Jolanta Bukowska. After postdoctoral work in theoretical chemistry with Roald Hoffmann (Cornell, US), and in experimental inorganic and materials chemistry with Peter P. Edwards (Birmingham, UK) he returned to Poland. He obtained his habilitation at the University of Warsaw in 2005, and in 2011 he was appointed Full Professor. Wojciech Grochala received the Kosciuszko Foundation Fellowship (US), Royal Society of Chemistry Postdoctoral and Research Fellowships (UK), The Crescendum est Polonia Foundation Fellowship (Poland), and Świętosławski Prize 2nd degree (Polish Chem. Soc., Warsaw section). In 2014 he was granted titular professorship from the President of Poland. Since 2005 Grochala heads the Laboratory of Technology of Novel Functional Materials, currently with some 30 group members. He has published more than 150 papers in reputed journals.

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