ION-PLAZMA VA LAZER TEXNOLOGIYALARI INSTITUTI HUZURIDAGI ILMIY DARAJALAR BERUVCHI DSc.02/30.12.2019.FM/T.65.01 RAQAMLI ILMIY KENGASH

ION-PLAZMA VA LAZER TEXNOLOGIYALARI INSTITUTI

ASHUROV ILXOMJON XATAM O'G'LI

ALYUMINIY AKKUMULYATORLARI UCHUN XONA HARORATIDAGI ION-SUYUQLIK ELEKTROLITLAR VA GRAFEN ASOSLI KATODLARNI EKSPERIMENTAL TADQIQ ETISH HAMDA KOMPYUTERDA MODELLASHTIRISH

01.04.12 – Nanomateriallar fizikasi va texnologiyasi

fizika-matematika fanlari bo'yicha falsafa doktori (PhD)

AVTOREFERATI

TOSHKENT-2025

UDK: 538.975; 535.3; 620.3; 539.2;

Fizika va matematika fanlari bo‘yicha falsafa doktori (PhD) dissertatsiyasi avtoreferati mundarijasi

Оглавление автореферата диссертаци доктора философии (PhD) по физико-математическим наукам

Contents of dissertation abstract of doctor of philosophy (PhD) on physics and mathematics sciences

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Fizika va matematika fanlari bo‘yicha falsafa doktori (PhD) dissertatsiyasi mavzusi O‘zbekiston Respublikasi Oliy ta’lim, fan va innovatsiyalar vazirligi huzuridagi Oliy attestatsiya komissiyasida № B2025.3.PhD/FM1385 raqam bilan ro‘yxatga olingan.

Dissertatsiya O‘zR FA Ion-plazma va lazer texnologiyalari institutida bajarilgan.

Dissertatsiya avtoreferati uch tilda (o‘zbek, ingliz va rus) Ilmiy kengash web - sahifasida (www.iplt.uz) hamda «ZiyoNet» axborot-ta’lim portalida (www.ziyonet.uz) joylashtirilgan.

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Dissertatsiya himoyasi Ion-plazma va lazer texnologiyalari instituti huzuridagi ilmiy darajalar beruvchi DSc.02/30.12.2019.FM/T.65.01 raqamli ilmiy kengashning 2025 yil «11» dekabr soat 14:30 dagi majlisida bo‘lib o‘tadi. (Manzil: 100125, Toshkent shahri, Do‘rmon yo‘li ko‘chasi, 33-uy. Tel./faks: (99871) 262-32-54, e-mail: info@iplt.uz, Ion-plazma va lazer texnologiyalari instituti).

Dissertatsiya bilan Ion-plazma va lazer texnologiyalari institutining Axborot-resurs markazida tanishish mumkin (21-raqam bilan ro‘yxatga olingan). (Manzil: 100125, Toshkent shahri, Do‘rmon yo‘li ko‘chasi, 33-uy. Tel: (99871) 262-31-69.)

Dissertatsiya avtoreferati 2025 yil «02» dekabr kuni tarqatildi.
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KIRISh (falsafa doktori (PhD) dissertatsiya annotasiyasi)

Dissertatsiya mavzusining dolzarbligi va zarurati: So‘nggi o‘n yilliklarda qayta tiklanadigan energiya manbalarining integratsiyasi, elektrlashtirilgan transport tizimiga o‘tish va barqaror materiallar aylanmasini ta’minlashga qaratilgan jadal global siljish zamonaviy elektrokimyoviy energiya saqlash tizimlariga bo‘lgan ehtiyojni keskin kuchaytirdi. Elektromobillar, tarmoqni barqarorlashtirish, ko‘chma elektron qurilmalar va atrof-muhit monitoringi kabi yo‘nalishlar yuqori samaradorlik, ekspluatatsion xavfsizlik, uzoq xizmat muddati va eng muhimi, yer yuzasida keng tarqalgan elementlardan foydalanishni birlashtira oladigan akkumulatorlarni talab qiladi. Bu talablarni qondirish yangi elektrod materiallarini, optimallashtirilgan elektrolitlarni hamda ilg‘or xarakterlash va modellashtirish usullarini muntazam ravishda rivojlantirishni taqozo etadi.

Rivojlanayotgan post-litiy kimyoviy elementlari orasida alyuminiy dual-ionli akkumulatorlar (ADIA) barqarorlik va iqtisodiy samaradorlik nuqtayi nazaridan muqobil yechim sifatida katta e’tiborga sazovor bo‘lmoqda. Alyuminiy – yer qobig‘idagi eng keng tarqalgan metall bo‘lib, arzonligi, zaharsizligi, yuqori hajmiy sig‘imi va yaxshi qayta ishlanuvchanligi tufayli keyingi avlod energiya saqlash tizimlari uchun ideal nomzoddir. $AlCl_3$ 1- etil-3-metilimidazoliy xlorid (EMImCl) asosidagi Lyuis-kislotali elektrolitlarda ADIAlar dual-ionli elektrokimyoviy mexanizm bo‘yicha ishlaydi: anodda metall alyuminiy $Al_2Cl_7^-$ /Al redoks juftligi orqali qaytar tarzda cho‘ktiriladi va eritiladi, katodda esa murakkab xloroalyuminat anionlari ($AlCl_4^-$) qatlamli sp^2- uglerod strukturalarining qatlamlari orasiga kiritiladi (interkalyatsiyalanadi) va chiqariladi (deinterkalyatsiyalanadi). Ushbu tizimda grafit va bog‘lovchisiz grafen qog‘ozi yuqori salohiyatli katod materiallari sifatida ajralib turadi. Ularning yuqori elektr o‘tkazuvchanligi, tartibli strukturasi va mexanik egiluvchanligi $AlCl_4^-$ anionlarining qatlamlanishi (steydjing) jarayonida ion-elektronlarning tez tashilishini va qatlamlararo masofaning yanada kengayishini ta’minlaydi. Xususan, bog‘lovchisiz grafen qog‘ozi yengil, tok kollektorini talab qilmaydigan (collector-free) va yuqori o‘tkazuvchanlikka ega bo‘lib, qisqa diffuziya yo‘llari, ko‘p qirra va nuqson joylari, shuningdek, yuqori mexanik yaxlitlikni ta’minlaydi. Bu esa an’anaviy grafit elektrodlarga nisbatan tezkor zaryadlanish-razryadlanish qobiliyatini oshirishga, polyarizatsiyani kamaytirishga va sikl barqarorligini uzaytirishga xizmat qiladi.

Alyuminiy dual-ionli akkumulatorlarning umumiy ish samaradorligi bir nechta o‘zaro bog‘liq omillar, jumladan, elektrolitning ion tarkibi ($AlCl_3$:[EMImCl] molyar nisbati orqali boshqariladi), katodning mikrostrukturaviy xususiyatlari (g‘ovaklik, qalinlik, qatlamlararo oraliq va egrilik darajasi) hamda katod–elektrolit chegarasidagi kimyoviy dinamika bilan belgilanadi. Shu bois, elektrolitning tarkibi, elektrodning tuzilishi va chegaradagi jarayonlar o‘rtasidagi bog‘liqliklarni aniqlash uchun eksperimental va hisoblash (kommunikatsion) usullarni birlashtirgan kompleks tadqiqot o‘tkazish zarurdir. Bu kabi chuqur va keng qamrovli tushuncha barqaror va xavfsiz elektrokimyoviy energiya saqlashga bo‘lgan global ehtiyojni qondirishga qodir bo‘lgan yuqori samarali, chidamli va miqyoslanadigan ADIAlarning asosli dizayni uchun mustahkam ilmiy poydevor yaratadi.

Ushbu tadqiqot ishi O‘zbekiston Respublikasi Prezidentining 2022-yil 28-yanvardagi “2022 - 2026 - larda yangi O‘zbekistonni rivojlantirish strategiyasi to‘g‘risida”gi PF-60-sonli Farmoni, 2017-yil 17-fevraldagi “Fanlar akademiyasi faoliyatini yanada takomillashtirish, ilmiy-tadqiqot ishlarini tashkil etish, boshqarish va moliyalashtirish chora-tadbirlari to‘g‘risida”gi PF-2789-sonli Farmoni va 2019-yil 22-avgustdagi “Xo‘jalik va maxsus sohalarda energiya samaradorligini oshirish, energiyani tejash texnologiyalarini joriy etish va qayta tiklanadigan energiya manbalarini rivojlantirish bo‘yicha tezkor choralar to‘g‘risida”gi PF-4422-sonli Farmonlarida belgilangan vazifalarning amalga oshirilishiga hissa qo‘shadi.

Tadqiqotning respublika fan va texnologiyalari rivojlanishining ustuvor yo‘nalishlariga mosligi: Ushbu tadqiqot O‘zbekiston Respublikasining energetika samaradorligi, qayta tiklanadigan energiya manbalarini integratsiya qilish va ilg‘or materialshunoslik sohalaridagi strategik ustuvor yo‘nalishlariga to‘liq mos keladi. Bu ish xavfsiz, chidamli va ishlab chiqarishga mos keluvchi elektrokimyoviy energiya saqlash tizimlarini rivojlantirish orqali mamlakatimizning barqaror texnologik rivojlanish borasidagi milliy maqsadlariga hissa qo‘shadi. Bu esa, o‘z navbatida, kam uglerodli va resurslarni tejovchi iqtisodiyotga o‘tishni osonlashtiradi.

Muammoning o‘rganilganlik darajasi: Global miqyosda alyuminiy asosli dual-ionli va alyuminiy-ionli akkumulatorlar bo‘yicha tadqiqotlar yetakchi akademik guruhlar va tijorat korxonalari tomonidan faol olib borilmoqda. Jumladan, Hongji Day guruhi (Stanford University/SLAC) yuqori tezlikdagi alyuminiy–grafit elementlariga asos solib, xloroalyuminatning interkalyatsiyasini operando Raman tadqiqotlari yordamida birinchilardan bo‘lib o‘rgangan. Helmholtz Institute Ulm/ Karlsruhe Institute of Technology (KIT) hamkor tashkilotlar bilan birgalikda uglerod asosdagi materiallarning qatlamlanish va degradatsiya jarayonlarini tahlil qilish uchun operando XRD, tomografiya va modellashtirishni muvaffaqiyatli qo‘llagan.

University of Queensland(UQ)/Graphene Manufacturing Group (GMG) hamkorligi grafenli alyuminiy-ionli akkumulator prototiplari ustida ishlab, Battery Innovation Center (Indiana, AQSH) bilan sheriklikda tijoratlashtirishga intilayotgan sanoqli loyihalardan biridir. Yevropada esa Albufera Energy Storage (Ispaniya) alyuminiy-ionli element prototiplarini yaratmoqda va barqaror akkumulator ishlab chiqarishni miqyoslash yo‘llarini ilgari surmoqda. Germaniya, Shveysariya (masalan, Empa) va Fransiyadagi bir qator tadqiqot guruhlari ilg‘or uglerod katodlar va ion suyuqliklarni faol o‘rganib, ko‘pincha in-situ/operando spektroskopiyani uzluksiz modellashtirish (continuum modeling) bilan bog‘lamoqda. Materialshunoslik sohasidagi yangilik sifatida, Ursula Krossing guruhi (University of Freiburg / Ulm) yaqinda alyuminiy-ion tizimlari uchun organik redoks polimer katodlarni tatbiq etdi va muqobil katod kimyosida uzaytirilgan sikllarni namoyish qildi. Bundan tashqari, MacDiarmid Institute (Yangi Zelandiya/Avstraliya) tadqiqotchilari tomonidan asos solingan TasmanIon akademik doiralarda ishlab

chiqilgan alyuminiy-ionli akkumulator texnologiyasini tijoratlashtirishga harakat qilmoqda.

Shunga qaramay, hozirgacha olib borilgan tadqiqotlarning aksariyati alohida qismlarga bo‘linib qolgan. Ular elektrolit tarkibi, uglerod arxitekturasi yoki operando usullariga alohida-alohida e’tibor qaratgan. Ayniqsa, sp^2 -uglerod asosli katodlarni o‘z ichiga olgan alyuminiy dual-ionli tizimlar uchun juda kam guruhlar uch o‘lchovni (elektrokimyoviy ish faoliyati, strukturaviy dinamika va hisoblash modellashtirishni) yagona, o‘zaro tasdiqlangan tadqiqot doirasiga birlashtira olgan. Ana shunday kompleks yondashuvdagi bo‘shliq mazkur ishning keng qamrovli, mexanizmga asoslangan va fanlararo tadqiqot strategiyasini asoslaydi.

Dissertatsiya tadqiqotining dissertatsiya bajarilgan ilmiy tadqiqot muassasasining ilmiy tadqiqot ishlari bilan bog‘liqligi: Dissertatsiya ishi Ion-plazma va lazer texnologiyalari institutining ilmiy-tadqiqot ishlar rejasiga muvofiq, IL-5421101842 “Nanokatalizatorlar: shakillanishi, strukturasi, o‘lchov effektlari va ularning uglerod nanomateriallari sintezi jarayonlariga ta’siri” nomli fundamental loyihasi doirasida bajarilgan.

Tadqiqotning maqsadi: ADIA tizimini optimallashtirish uchun elektrolit kislotaliligi, ion tarkibi, uglerod asosli katodning arxitekturasi va katod–elektrolit chegarasidagi barqarorlikni kompleks o‘rganish orqali mexanizmga asoslangan ilmiy yondashuvni ishlab chiqishdan iborat.

Tadqiqotning vazifalari:

- bindersiz grafen qog‘ozi va grafit kompozitli katodlarini tayyorlash, shuningdek ularning elektrokimyoviy xususiyatlarini taqqoslash orqali interkalatsiya mexanizmini tahlil qilish va akkumulyator uchun eng optimal elektrod materialini tanlab olish;
- $AlCl_3$:[EMIm]Cl asosidagi ion-suyuqlik elektrolitlarini 1.3:1, 1.5:1 va 1.7:1 molyar nisbatlarda tayyorlab, ularning Lyuis kislotaligi va ion tarkibining shakllanishini boshqarish orqali elektrolit xususiyatlarini optimallashtirish;
- Swagelok va paketli geometriyaga ega bo’lgan Al/grafen va Al/grafit yacheykalarini yig‘ish hamda ularni CV (siklik voltammetriya), EIS (elektrokimyoviy impedans spektroskopiyasi) va GCPL (potentsial bilan cheklangan galvanostatik zaryadlash) sinovlari orqali tekshirish;
- qayta zaryad–razryad jarayonlari davomida yuzaga keladigan qatlamlararo masofaning kengayishi va aniq bosqichlanish (staging) shakllanishini kuzatish orqali ex-situ XRD yordamida $AlCl_4^-$ ionlarining interkalatsiya mexanizmini o‘rganish;
- ex-situ Raman spektroskopiyasi yordamida strukturaviy va mexanik o‘zgarishlarni tahlil qilish, shuningdek qatlamlararo kengayish natijasida hosil bo‘ladigan stresslarni baholash. Olingan natijalarni COMSOL Multiphysics yordamida modellashtirish;
- ADIA uchun optimallashtirilgan Swagelok yacheykalarining natijalaridan kelib chiqib, paketli geometriyaga ega bo’lgan prototiplarni ishlab chiqish va ularni kompleks tahlillar bilan integratsiya qilish;

- elektrolit tarkibi va katod arxitekturasini bog‘laydigan amaliy dizayn ko‘rsatmalarini ishlab chiqish. Bu, o‘z navbatida, yuqori samarali, chidamli va ishlab chiqarishga mos keladigan energiya saqlash tizimlari uchun alyuminiy dual-ionli akkumulatorlarni oqilona miqyoslashga imkon berish.

Tadqiqotning ob’ekti: $AlCl_3$:[EMImCl] ionli suyuq elektrolitlari, grafit va bog‘lovchisiz grafen-qog‘ozi katodlari, laboratoriya miqyosidagi alyuminiy dual-ionli Swagelok va paketli geometriyaga ega yacheykalar.

Tadqiqot predmeti: $AlCl_4^-$ anionlarining karbon katodlariga elektrokimyoviy interkalyatsiyasi va qatlamlanish jarayonlari. Ushbu jarayonlarning elektrolitning ion tarkibi va chegaraviy kimyo bilan o‘zaro bog‘liqligi; G‘ovak elektroddagi ion tashilishi. Interkalyatsiya tufayli yuzaga keladigan deformatsiyasi.

Tadqiqotning usullari: Elektrokimyoviy usullar – CV, EIS va GCPL o‘lchovlari standartlashtirilgan sharoitlarda, iR-kompensatsiya va tok normallashtirilishi bilan amalga oshirildi. Bu usullar kinetik xususiyatlarni, zaryad tashilishi qarshiligini va qaytarlik (reversibility) darajasini baholash uchun qo‘llanildi.

Strukturaviy va yuzani xarakterlash - Rentgen difraksiyasi (XRD) akslanish (reflection), kapillyar va o‘ta yupqa qatlam rejimlarida, Raman spektroskopiyasi, hamda energiya tarqatuvchi spektroskopiyali skanerlovchi elektron mikroskopiya (SEM/EDS) faza tarkibini, panjara parametrlarini, morfologiyani va elementlarning taqsimlanishini o‘rganish uchun ishlatildi.

Modellashtirishi - COMSOL Multiphysics dasturida ko‘pfizikali simulyatsiyalar o‘tkazildi. Bu simulyatsiyalar grafen-qog‘oz laminatlarida elektrolit diffuziyasi, interkalyatsiya tufayli yuzaga keladigan deformatsiya va kuchlanish (stress) evolyutsiyasini modellashtirishga qaratilgan.

Tadqiqotning ilmiy yangiligi:

- ilk bor, tijoratlashtirilgan, binder ishlatilmagan grafen qog‘ozi katod sifatida ADIAda foydalanildi va bu an’anaviy elektrodlar uchun xos bo‘lgan murakkab ko‘p bosqichli elektrod tayyorlash jarayonini soddalashtirib, elektrokimyoviy faol bo‘lmagan komponentlarni butunlay bartaraf etdi;
- ilk bor bindersiz grafen qog‘ozi va grafit kompozitidan tashkil topgan katod materiallari xona haroratidagi ion-suyuqlik elektrolitlarining turli $AlCl_3$:[EMIm]Cl molyar nisbatlarida tizimli ravishda elektrokimyoviy baholab chiqildi. Ushbu kompleks tahlil orqali elektrod–elektrolit o‘zaro ta’sirining asosiy qonuniyatlari aniqlanib, akkumulyatorning optimal ishlashini ta’minlaydigan eng maqbul elektrolit tarkibi belgilandi;
- ilk bor ex-situ XRD va Raman spektroskopiyalari natijalari Comsol Multiphysicsdagi Solid Mechanics modulining hisoblashlari bilan intergratsiyalangan holda qo’llanilib, zaryad-razryad sikllari davomida yuzaga keladigan strukturaviy o’zgarishlar hamda mexanik stresslarning katod arxitekturasiga potensial ta’siri aniq baholandi. Ushbu kompleks

yondashuv elektrod materialining mexanik va elektrokimyoviy barqarorligini chuqur va ko’p omilli tahlil qilish imkonini yaratdi;

- ilk bor modellashtirish natijalari va eksperimental kuzatuvlarga asoslangan optimallashtirilgan yacheyka strukturasining ishlab chiqilishi mexanik moslashuvchanlik va elektrokimyoviy samaradorlikni birlashtirgan paketli geometriyaga ega ADIA yacheykalarini yaratish yo‘lida muhim ilmiy bosqich sifatida namoyon bo‘ldi.

Tadqiqotning amaliy natijalari.

ADIAlar uchun standartlashtirilgan laboratoriya protokollari ishlab chiqildi. Bu protokollar Swagelok tipidagi hamda paket tipidagi element konfiguratsiyalari uchun qo‘llanilib, barcha eksperimental bosqichlarda qayta takrorlanuvchi yig‘ishni, ishonchli sinovni va izchil elektrokimyoviy baholashni ta’minlaydi. Eksperimentlar davomida aniqlangan ionik va strukturaviy asoslarni yumshatish maqsadida bog‘lovchisiz grafen-qog‘ozi katodlari uchun arxitekturaviy dizayn ko‘rsatmalari shakllantirildi. Ushbu ko‘rsatmalar ko‘p qatlamli grafen laminatlarida ion tashilishining bir xilligini, mexanik yaxlitlikni va elektrokimyoviy o‘tkazuvchanlikni yaxshilaydi, shu bilan birga, takrorlanuvchi elektrod ishlab chiqarish uchun asos yaratadi. Fundamental Swagelok-yacheyka o‘lchovlaridan laboratoriya miqyosidagi paketli yacheyka prototiplariga o‘tishni qo‘llab-quvvatlash uchun miqyoslash (scale-up) qabul mezonlari o‘rnatildi. Bu tizimli ish samaradorligini baholash va sinov konfiguratsiyalari o‘rtasidagi o‘zgaruvchanlikni minimallashtirish imkonini beradi. Elektrolit–katod muvofiqligi mezonlari $AlCl_3$:[EMImCl] tizimi uchun aniqlandi. Bu mezonlar nazorat qilinadigan laboratoriya sharoitlarida ADIA elementlarida barqaror ishlashni, qutblanishni minimallashtirishni va ishonchli sikl umrini ta’minlash uchun optimal tarkiblar va karbon arxitekturalarini belgilab berdi.

Tadqiqot natijalarining ishonchliligi: Olingan natijalarning ishonchliligi etalon standartlarga muvofiq tizimli kalibrlash, elektrokimyoviy o‘lchovlarni takrorlash va eksperimental ma’lumotlarning statistik ishonch tahlili orqali ta’minlanadi. Strukturaviy va elektrokimyoviy xulosalar o‘zaro tasdiqlandi. Bu XRD, Raman, SEM/EDS, CV, EIS va GCPL natijalari o‘rtasidagi ichki muvofiqlikni tasdiqladi. Hisoblash modellashtirishi esa to‘rning konvergensiya sinovlari (mesh convergence tests), yechimning sezgirlik tahlili (solution sensitivity analysis) va eksperimental kuzatuvlar bilan miqdoriy taqqoslash orqali verifikatsiya qilindi, bu esa ishlab chiqilgan asosning mustahkamligi va takrorlanuvchanligini (reproducibility) tasdiqlaydi.

Tadqiqot natijalarining ilmiy va amaliy ahamiyati: O‘tkazilgan tadqiqot elektrokimyoviy energiya saqlash sohasiga jiddiy ilmiy hissa qo‘shadi. U ADIAlar ish faoliyatiga elektrolit kislotaliligi, anion tarkibi va uglerod asosli katod arxitekturasining o‘zaro bog‘liq ta’sirini chuqur tahlil qilib, oydinlashtirib beradi.

Elektrokimyoviy diagnostika, strukturaviy xarakterlash va ko‘pfizikali modellashtirishni integratsiya qilish bog‘lovchisiz grafen-qog‘ozi elektrodlaridagi ionlarning qatlamlanishi (staging), chegaraviy o‘zgarishlar va kimyo-mexanik

xususiyatlarni tavsiflovchi mexanizmga asoslangan asosni shakllantirishga imkon berdi. Bu natijalar ko‘p valentli ionlarning interkalyatsiya dinamikasi haqidagi mavjud tushunchalarni kengaytiradi va ilg‘or uglerod asosli energiya saqlash materiallarini loyihalash uchun umumlashgan konseptual asos yaratadi. Amaliy nuqtayi nazardan, ushbu tadqiqot nazorat qilinadigan sharoitlarda elektrolit–katod tizimlarini baholash uchun muvofiqlashtirilgan laboratoriya metodologiyalari va optimallashtirish mezonlari to‘plamini o‘rnatadi. Ishlab chiqilgan grafen-qog‘ozi arxitekturasi bo‘yicha ko‘rsatmalar va masshtablashtirish mezonlari laboratoriya miqyosidagi ADIAlarni yig‘ish va ish faoliyatini baholash uchun takrorlanuvchi tayanch nuqtalarini taqdim etadi.

Bundan tashqari, eksperimental ma’lumotlarga asosan tasdiqlangan COMSOL Multiphysics simulyatsiya asosi keng doiradagi ko‘p valentli elektrokimyoviy tizimlarda tashilish va mexanikaning o‘zaro bog‘liqligini tahlil qilish uchun ko‘chirib o‘tkazish mumkin bo‘lgan modellashtirish vositasi hisoblanadi.

Tadqiqot natijalarining joriy qilinishi:

Dissertatsiya tadqiqotlari doirasida olingan ilmiy natijalar “VV-LAND” MChJ bilan hamkorlikda ishlab chiqilgan “Elektroskuter akkumulyator modullarining zaryad razryad barqarorligini ta’minlash, GCPL diagnostikasi va xizmat muddatini uzaytirish bo‘yicha texnik reglament” (№ 27/10-2025) loyihasi doirasida muvaffaqiyatli amaliyotga joriy etildi. Mazkur yechimlar akkumulyatorlar uchun optimal zaryad holatini (SoC 40–80 %) belgilash, elementlar o‘rtasidagi passiv balanslash jarayonining barqarorligini oshirish, shuningdek GCPL va EIS metodlari asosida degradatsiya jarayonlarini erta aniqlashga imkon beradi. Ushbu ilmiy-texnik ishlanmalarning amaliyotga tatbiq etilgani “VV-LAND” MChJ tomonidan taqdim etilgan rasmiy hujjat orqali tasdiqlangan.

Alyuminiy-ionli akkumulyatorlarning dolzarb muammolari, yutuqlari va kelajak istiqbollariga bag’ishlangan maqola: “Current challenges, progress and future perspectives” (Applied Solar Energy, Applied Solar Energy, 2022, Vol. 58, No. 3, pp. 334–354. DOI: 10.3103/S0003701X22030033) natijalariga xalqaro tadqiqotchilar tomonidan, qator maqolalarda (J. Chai et al, Energy Storage Materials, 81, 2025), H. Zhao et al. Advanced Functional Materials, 2025), R. Afian et al. Journal of the Physical Society of Indonesia, 1, 2025, A. Borozdin et al. Russian Metallurgy, 2, 2025, Y. Zhou va et al. Energy Technology, 13(4), 2024 hamda M. Saghir et al. Applied Solar Energy, 60(3), 2024) havola qilingan.

Tadqiqot natijalarining aprobasiyasi: mazkur tadqiqotning natijalari 4 ta xalqaro ilmiy-texnik va ilmiy amaliy anjumanlarda aprobatsiyadan o‘tkazilgan.

Tadqiqot natijalarining e’lon qilinganligi: dissertatsiya mavzusi bo‘yicha jami 5 ta ilmiy ish chop etilgan, O‘zbekiston Respublikasi Oliy Attestatsiya Komissiyasining dissertatsiyalarning asosiy ilmiy natijalarini chop etish tavsiya etilgan ilmiy nashrlarda 5 ta, jumladan 2 ta xorijiy va 3 ta respublika ilmiy jurnallarda nashr etilgan.

Dissertatsiya tuzilishi va hajmi: dissertatsiya tarkibiy tuzilishi kirish, beshta bob, xulosa, 265 ta foydalanilgan adabiyotlar ro‘yxatidan iborat. Dissertatsiyaning xajmi 122 betni tashkil etadi, 41 ta rasm va 3 ta jadval mavjud.

DISSERTATSIYANING ASOSIY MAZMUNI

Dissertatsiyaning kirish qismida tadqiqot mavzusining muhimligi va dolzarbligi asoslangan, maqsadi va vazifalari shakllantirilgan, obyekt, predmet va tadqiqot usullari belgilangan. Shuningdek, ishning O‘zbekiston Respublikasining ilmiy-texnologik rivojlanishining ustuvor yo‘nalishlariga mosligi asoslangan. Bundan tashqari, ilmiy yangiligi va amaliy ahamiyati belgilangan, ma’lumotlarning ishonchliligi ko‘rsatilgan, amaliyotga tatbiqi va aprobatsiyasi bayon etilgan hamda dissertatsiyaning umumiy tuzilmasi taqdim etilgan.

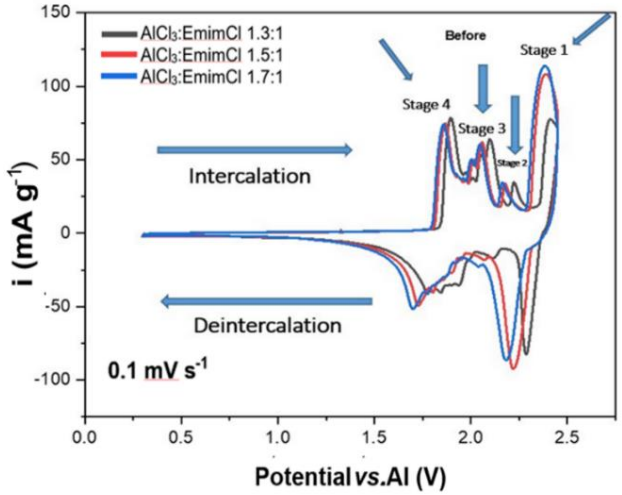
Dissertatsiyaning birinchi bobida uglerod asosidagi katodlar, grafit va grafen materiallari qo‘llanilgan ADIAlar bo‘yicha adabiyotlarning tanqidiy sharhini taqdim etadi. Muhokama asosan qatlamli uglerod materiallaridagi $AlCl_4^-$ anionining interkalyatsiyasi va qatlamlanish mexanizmlariga qaratiladi. Tahlil elektrolit tarkibini va uning Lyuis kislotaligini $AlCl_3$:[EMImCl] molyar nisbatlari orqali elektrokimyoviy reaksiya bilan bog‘laydi. Shu bilan birga, qaytaruvchanlik va sikl barqarorligini oshiruvchi omillar sifatida yuqori elektr o‘tkazuvchanlik hamda ionlar oson kirib-chiqa oladigan qatlamlararo bo‘shliqlar kabi strukturaviy xususiyatlar alohida ta’kidlanadi. Katod modifikatsiyasi, chegaraviy fazani boshqarish va elektrolitni optimallashtirish bo‘yicha yutuqlar umumlashtiriladi va eksperimental hamda modellashtirish dasturini shakllantirish uchun mavjud bilim bo‘shliqlari aniqlanadi.

Dissertatsiyaning ikkinchi bobida tadqiqotda qo‘llanilgan materiallar va usullarni batafsil yoritadi. Jumladan, uglerod saji va λ-karragenan bog‘lovchisi yordamida karbon qog‘oz asosida grafit elektrodlarni tayyorlash, shuningdek, bog‘lovchisiz grafen qog‘ozi katodlarini hosil qilish jarayonlari bayon etilgan. Bundan tashqari, turli molyar nisbatlarda qat’iy angidrus (suvsiz) $AlCl_3$:[EMImCl] elektrolitlarini tayyorlash tartibi hamda CV, EIS va GCPL sinovlarini o‘tkazish uchun standartlashtirilgan parametrlar — potensial oraliqlari, skanerlash tezliklari va normallashtirish protokollari aniq ko‘rsatilgan holda tavsiflangan. XRD, Raman spektroskopiyasi, SEM/EDS yordamida strukturaviy va morfologiyani xarakterlash asosiy analitik parametrlar bilan birga ta’riflanadi. Grafen-qog‘ozi katodlaridagi ionik tashilishni kimyo-mexanik reaksiyalar bilan bog‘laydigan COMSOL Multiphysics ish oqimi tanishtiriladi.

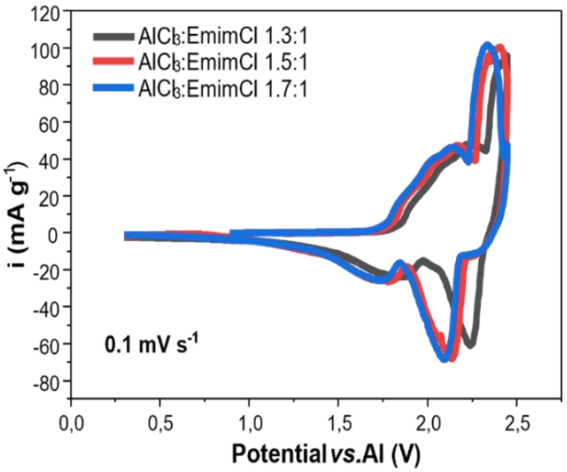
Uchinchi bob “ADIA elektrolitida grafen qog‘ozi va grafit katodlarining elektroximiyoviy xarakteristikasi va natijalari” eksperimental natijalar rasmlar ketma-ketligida taqdim etilgan bo‘lib, bu yerda elektrokimyoviy xususiyatlar elektrolitning kislotaligi, katod arxitekturasi hamda bog‘langan tashilish-mexanik effektlar bilan o‘zaro bog‘liq holda tahlil qiliqilingan.

3.1-rasmda $AlCl_3$:[EMImCl] nisbatlari 1.3:1 (qora chiziq), 1.5:1 (qizil chiziq) va 1.7:1 (ko‘k chiziq) bo‘lgan holdagi grafitning CV natijalari (0.30–2.45 V vs Al) keltirilgan bo‘lib, ular ko‘p bosqichli qatlamlanish jarayonini hamda unga mos katod jarayonlarini aniq namoyon etadi. Lyuis kislotaligining ortishi cho‘qqilarni o‘tkirlashtiradi va yaxshiroq ajratadi, anod-katod siljishini qisqartiradi hamda cho‘qqilar orasidagi bazaviy chiziqni deyarli yassi holda saqlaydi. Anod jarayonlari taxminan 2.03, 2.20–2.26, 2.31–2.35 va 2.42–2.45 V (Stage-1 boshlanishi) atrofida

kuzatiladi, katod jarayonlari esa taxminan 30–70 mV past potensiallarda joylashgan. Cho‘qqilar toki 60 mA· g^{-1} dan 110 mA· g^{-1} gacha ortadi, gisterezis esa 80–100 mV dan taxminan 30–50 mV gacha qisqaradi. Bu esa yuqoriroq almashinuv tok zichligi (i_0) hamda zaryad almashinuv va massa tashilishi cheklovlarining kamayishini ko‘rsatadi.



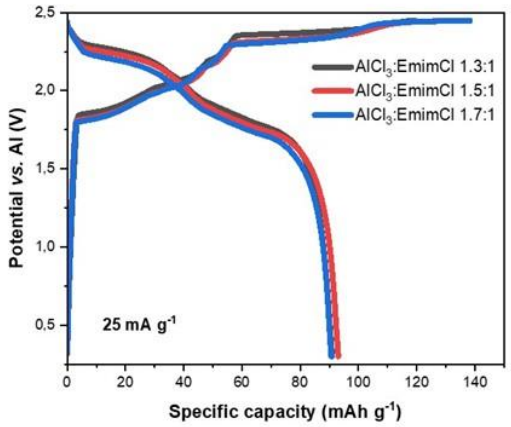
3.1-rasm. $AlCl_3$:EMImCl (1.3:1–1.7:1) elektrolitdagi grafitning CV: kislotalik oshishi bilan $AlCl_4^-$ interkalyatsiyasi va gisterezisning kamayishi



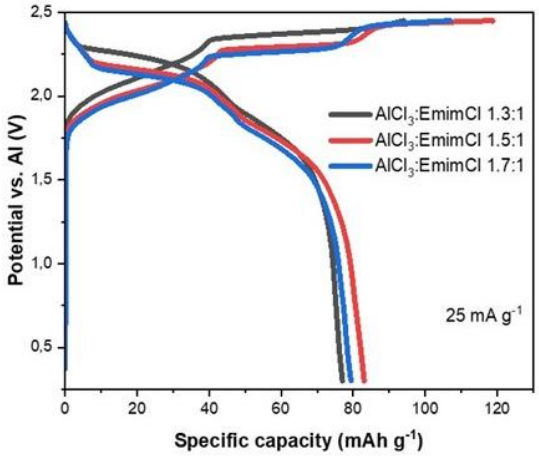
3.2-rasm. Grafen qog‘ozi uchun CV tahlili: kislotalik oshishi bilan bosqichlanish (staging) o‘zgarishi

3.2-rasmda $AlCl_3$:[EMImCl] elektrolitlaridagi grafen qog‘ozi elektrodining qo‘shma (overlaid) CV cho‘qqilari keltirilgan bo‘lib, ular kislotalik ortishiga nisbatan qat’iy monoton reaksiyani namoyon etadi. Anod bosqichlanish o‘tishlari ozgina yuqoriroq potensial tomon siljiydi: Stage-4 — taxminan 2.05 → 2.07–2.09 V, Stage-3 — 2.20–2.23 → 2.23–2.26 V, Stage-2 — 2.31–2.33 → 2.34–2.36 V, va Stage-1 boshlanishi — taxminan 2.43–2.45 V. Shu bilan birga, mos katod jarayonlari 30–70 mV past potensiallarda kuzatiladi.

Cho‘qqilar torlashadi (FWHM taxminan 20–35 % ga qisqaradi) va kuchayadi (terminal i_p 1.3:1, 1.5:1 va 1.7:1 nisbatlar uchun mos ravishda 100 → 115 → 130–140 mA· g^{-1} ga yetadi), cho‘qqilar orasidagi bazaviy chiziq esa deyarli to‘g‘ri holda saqlanadi ($i \leq 1–2$ mA· g^{-1}). Qayta takrorlangan yoki turli skanerlash tezliklarida kapasitiv qoplama energiya signali kuzatilmagan. ΔE_p ning qisqarishi (~30–50 mV) va cho‘qqilar simmetriyasining yaxshilanishi almashinuv tok zichligining (i_0) oshganini va grafen qog‘ozli/elektrolit chegarasidagi energiya to‘siqlari taqsimotining torayganini ko‘rsatadi. Bu holat kislotalik ortishi bilan bog‘liq xlor-alyuminat spetsiyalashuvi (ion speciation) bilan mos keladi.



3.3-rasm. Grafit katodi uchun GCPL o‘lchovi

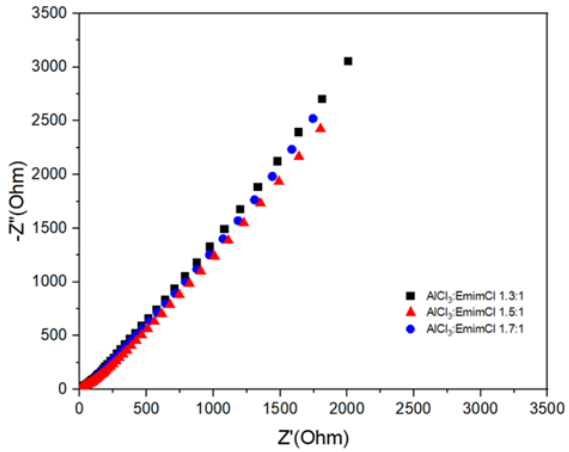


3.4-rasm. Grafen qog‘ozi uchun GCPL o‘lchovi

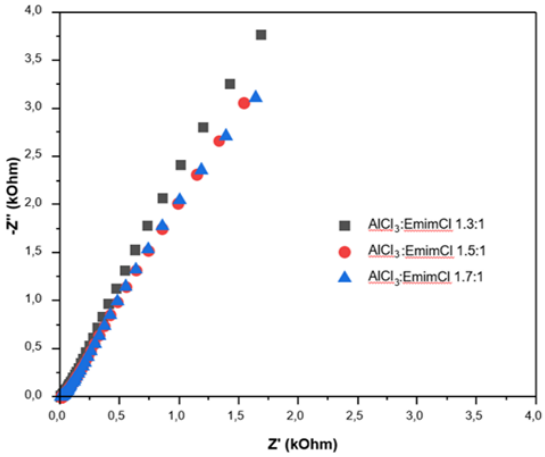
3.3-Rasmdagi galvanostatik profillar (25 mAh· g^{-1}), CV da aniqlangan qatlamlanish jarayonini takrorlaydi (dV/dQ bir necha millivolt aniqlikda mos keladi); bunda razryadlash 1.95–2.05 V oralig‘ida, zaryadlash esa 2.20–2.25 V da sodir bo‘ladi. Lyuis kislotaligini oshirish (1.3:1→1.7:1) natijasida kuchlanish oralig‘i 0.25 V dan 0.15 V gacha torayadi, deyarli yassi bazaviy chiziq saqlanib qoladi va sig‘im biroz oshadi (90 → 93 mAh· g^{-1}). Kichikroq iR sakrashi va pasaygan gisterezis pastroq Rs (seriyali qarshilik) va kamaygan ηct (zaryad tashilishi ortiqcha kuchlanishi) ni ko‘rsatadi; shunga muvofiq ravishda kuchlanish samaradorligi yaxshilanadi va takrorlashlarda barqarorlik saqlanadi.

3.4-rasmda ko‘rsatilganidek, bog‘lovchisiz grafen qog‘ozi laminatlangan grafitga nisbatan yassiroq va aniq bosqichlangan platolarni, shuningdek, kichikroq zaryad–razryad oralig‘ini namoyon etadi. Lyuis kislotaligi ortib borishi bilan (qora → qizil → ko‘k), razryad sig‘imi biroz oshadi (78 mAh· g^{-1} dan taxminan 82 mAh· g^{-1} gacha), gisterezis esa 0.30–0.33 V dan taxminan 0.18–0.20 V gacha qisqaradi. Grafen qog‘ozidagi plato darajalari biroz yuqoriroq va yassiroq bo‘lib, razryad jarayoni taxminan 1.92–2.02 V, zaryad jarayoni esa 2.18–2.23 V oralig‘ida kechadi; dV/dQ xususiyatlari esa ancha o‘tkir ko‘rinishga ega. Kislotalik darajasi ortishi cho‘qqilar orasidagi masofani qisqartiradi va platolar orasidagi o‘tishlarni silliqlashtiradi. Bu esa interfeysdagi zaryad almashinuv kinetikasining tezlashganini hamda qirralarga boy, bog‘lovchisiz grafen qog‘ozi arxitekturasidagi g‘ovak-transport yo‘qotishlarining kamayganini anglatadi.

3.5-rasm (Naykvist, grafen qog‘ozi): Yuqori chastotali kesish nuqtasi pasayishi (↓R_s) suyuqlikning yaxshi singishi va yuqori samarali o‘tkazuvchanlik (κeff) bilan bog‘liq. O‘rta chastotali bo‘rtgan duga qisqaradi va yuqoriroq xususiy chastota tomon siljiydi (↓Rct, ↑i_0, tarqalishning torayishi; CPE n↑). Past chastotali taxminan 45° burchakli Varburg dumi qisqargan va tikroq bo‘lib, bu samarali diffuziya koeffitsiyentining oshganini (↑D_{eff}) va tortiluvchanlikning (tortuosity) kamayganini ko‘rsatadi.



3.5-rasm. Grafen-qog‘ozining EIS tahlili

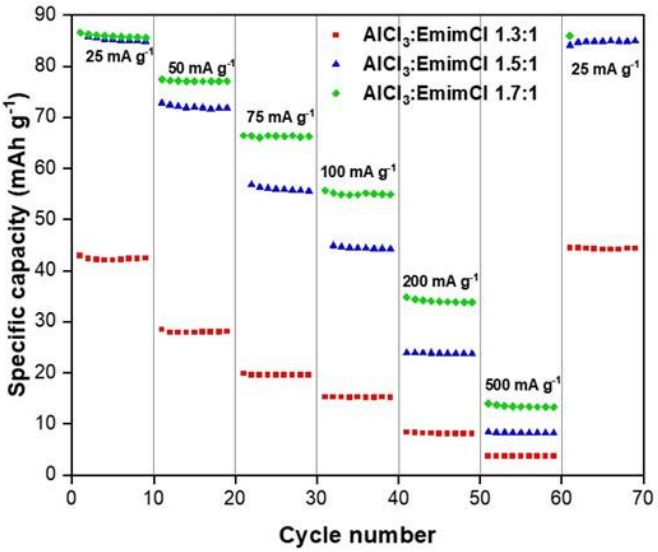


3.6-rasm. Grafit katodining EIS tahlili

Ekvivalent sxema bo‘yicha moslashtirish (R_s – (Rct ‖ CPE) – W) natijalarida ham R_s va Rct qiymatlari izchil pasayishi bilan birga interfeys sig‘imining biroz oshishi kuzatiladi. Bu esa CV cho‘qqilarining o‘tkirlashishi, platolarning moslashishi va GCPL gisterezisining kamayishi bilan muvofiq keladi.

3.6-rasm (Naykvist, grafit): grafen qog‘oziga o‘xshash kislotalik tendensiyasini namoyon etadi — R_s pasayadi, o‘rta chastotali duga kichrayib tezlashadi, va taxminan 45° Varburg dumi kuzatiladi, biroq barcha hollarda impedans qiymatlari yuqoriroq darajada qoladi. Ekvivalent sxema bo‘yicha moslashtirish (R_s – (Rct ‖ CPE) – W) natijalarida kattaroq R_s (suyuqlik singishining yomonligi / past κeff), kattaroq Rct (kichik i_0) va pastroq CPE ko‘rsatkichi n aniqlanadi, ammo bular kislotalik oshishi bilan izchil ravishda yaxshilanadi. Hatto eng yuqori kislotalikda ham R_s va Rct qiymatlari grafen qog‘oziga faqat yaqinlashadi, ammo to‘liq tenglashmaydi, Varburg chizig‘ining burchagi esa tikroq saqlanib qoladi. Bu holat to‘rli tuzilish (tortuosity) yuqoriligi va qirra kanallari soni kamligini ko‘rsatadi hamda asosiy kinetik boshqaruv omil sifatida ionli spetsiyalashuv (speciation) jarayonini belgilaydi. Shu bilan birga, elektrod arxitekturasi impedansning boshlang‘ich darajasini va qoldiq farqni (residual gap) belgilab turadi.

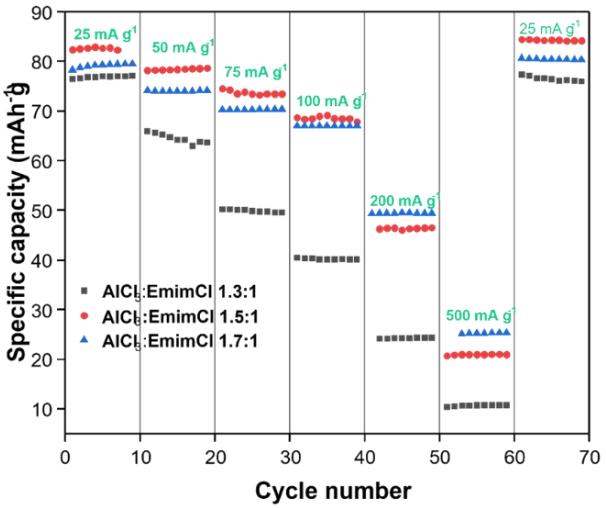
3.7-rasmda uch xil $AlCl_3$:[EMIm]Cl nisbatlaridagi grafit elektrodning tok zichligiga bog‘liq ishlash samaradorligi keltirilgan. Barcha hollarda tok zichligi oshgan sari sig‘im pasayadi, ammo 1.7:1 elektroliti 25 mA· g^{-1} da taxminan 85 mAh· g^{-1}, 500 mA· g^{-1} da esa 10–15 mA· g^{-1} sig‘imni saqlab qoladi. Bu holda platolar qisqaradi va ΔV ortib boradi, biroq interkalyatsiya potensiallari o‘zgarmaydi — bu termodinamik emas, balki kinetik cheklovlar bilan bog‘liqligini ko‘rsatadi. Tok yana 25 mA· g^{-1} ga qaytarilganda, sig‘im to‘liq tiklanib 85 mA· g^{-1} ga yetadi, bu esa qaytaruvchan polyarizatsiya mavjudligini tasdiqlaydi. CV va EIS natijalari bilan mos ravishda, 1.7:1 elektrolit eng yuqori samarali o‘tkazuvchanlik (κ_{eff}) va almashinuv tok zichligi (i_0) ko‘rsatib, yuqori toklarda ham eng yaxshi sig‘im saqlanishi va eng kichik ΔV o‘sishini ta’minlaydi.



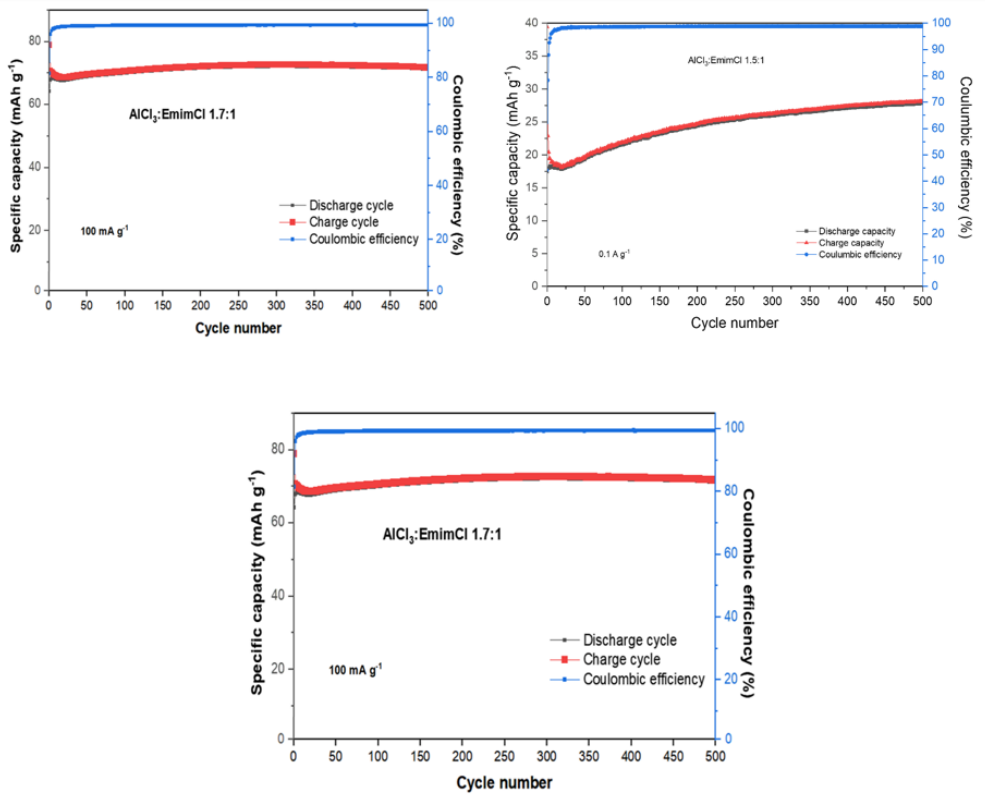
3.7-rasm. Grafit katodining turli elektrolit molyar nisbatlaridagi tokka chidamlilik (rate capability) natijalari

3.8-rasm (grafen qog‘ozi)da barcha tok zichliklari va elektrolit nisbatlarida grafitga nisbatan yuqoriroq sig‘im qiymatlari kuzatiladi. 25 mA· g^{-1} tok zichligida grafen qog‘ozi mos ravishda 76 (1.3:1), 78 (1.5:1) va 82 mA· g^{-1} (1.7:1) sig‘imni beradi, bu grafit elektrodga nisbatan bir xil sharoitlarda yuqoriroqdir. 500 mA· g^{-1} tok zichligida ham sig‘imni saqlab qolish qobiliyati ustunligini namoyon etadi: taxminan 27 (1.7:1) > 22 (1.5:1) > 10 mAh· g^{-1} (1.3:1). Demak, 1.7:1 elektrolit har ikki elektrod uchun ham eng tez kinetik javobni ta’minlaydi, grafen qog‘ozining o‘tkazuvchan va g‘ovak arxitekturasi esa yuqoriroq mutlaq sig‘im va yaxshiroq tokga chidamlilikni beradi. Tok zichligi yana 25 mA· g^{-1} ga qaytarilganda sig‘imning to‘liq tiklanishi bu holat degradatsiya emas, balki qaytaruvchan polyarizatsiya bilan izohlanishini tasdiqlaydi.

3.9-rasmda keltirilgan ma’lumotlarga ko‘ra, 1.3:1 nisbatda (100 mA· g^{-1}) grafen qog‘ozi taxminan 80 mA· g^{-1} sig‘imda barqaror holatga yetadi va zaryad samaradorligi (CE) 500 sikl davomida taxminan 99–100% gacha oshadi; zaryad va razryad oralig‘ining kichikligi yordamchi reaksiyalar kamligini hamda interfeysning barqarorligini ko‘rsatadi. 1.5:1 nisbatda (3.9b) razryad sig‘imi 35 mA· g^{-1} dan taxminan 25 mA· g^{-1} gacha pasayadi, biroq CE taxminan 80% dan ~99% gacha o‘sadi, bu esa ehtimolan ion tashilishi yoki kinetik jarayonlardagi cheklovlar yoxud interfeys qatlamining hosil bo‘lishi bilan bog‘liq. 1.7:1 nisbatdagi (3.9c) natijalar esa 70 mA· g^{-1} atrofidagi barqaror sig‘imni va CE ≈ 100% qiymatini ko‘rsatib, materialning uzoq muddatli barqarorligini tasdiqlaydi. Yuqori Lyuis kislotalik (1.7:1) zaryad almashinuv va ion tashilishi jarayonlarini 1.5:1 nisbatiga nisbatan yaxshilaydi, biroq 1.3:1 eng yuqori sig‘imni namoyon etadi, ehtimol, bu holat $AlCl_4^-$ ionlarining interkalyatsiya uchun optimal konsentratsiyasi bilan bog‘liq bo‘lib, pastroq kinetik tezlikka qaramasdan samarali ion kirishini ta’minlaydi.

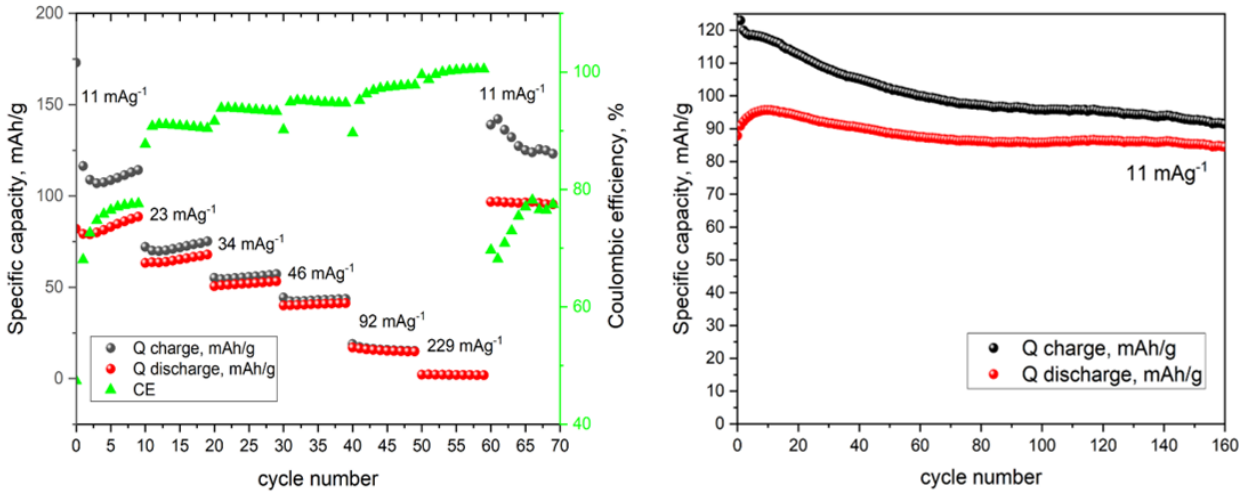


3.8-rasm. Grafen qog‘ozining turli elektrolit molyar nisbatlaridagi tokka chidamlilik (rate capability) natijalari



3.9-rasm. Grafen qog‘ozi elektrodi uchun uzoq muddatli barqarorlik sinovi

3.10a Rasmda ko‘rsatilganidek, va 3.10b Rasm tomonidan yanada tasdiqlanganidek, 1.7:1 nisbatdagi elektrolitga ega, bog‘lovchisiz grafen-qog‘ozidan tayyorlangan Pouch-element (xaltasimon element) qaytar terapevtik xususiyat va uzoq muddatli barqarorlikni namoyish etadi. 3.10a-Rasmda sig‘imlar tok oshgan sari pasayadi va tok 11 mA· g^{-1} ga qaytarilganda tiklanadi. Bunda Kuloniy samaradorligi (CE) ≈ 95–100% ni tashkil etadi, bu degradatsiyasiz, tashilish bilan cheklangan qutblanish mavjudligini bildiradi. 3.10b-Rasm esa 11 mA· g^{-1} tok zichligida ~160 sikldan ortiq muvozanatli (stable) sikl o‘tishini ko‘rsatadi.

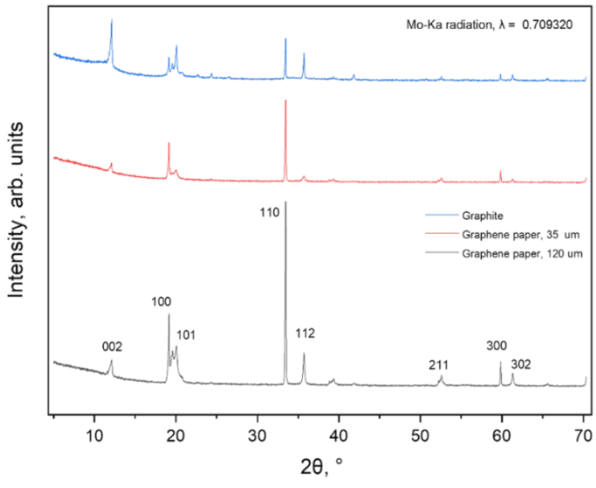


3.10 – rasm. Paket strukturali grafen qog‘ozining tokka chidamlilik va barqarorlik test sinovi

Bunda SE birlikka yaqin bo‘lib, sig‘im juda kam pasaygan. Bu yumshoq kinetik sharoitlarda yuqori qaytarlik va barqaror chegaraviy faza mavjudligini tasdiqlaydi.

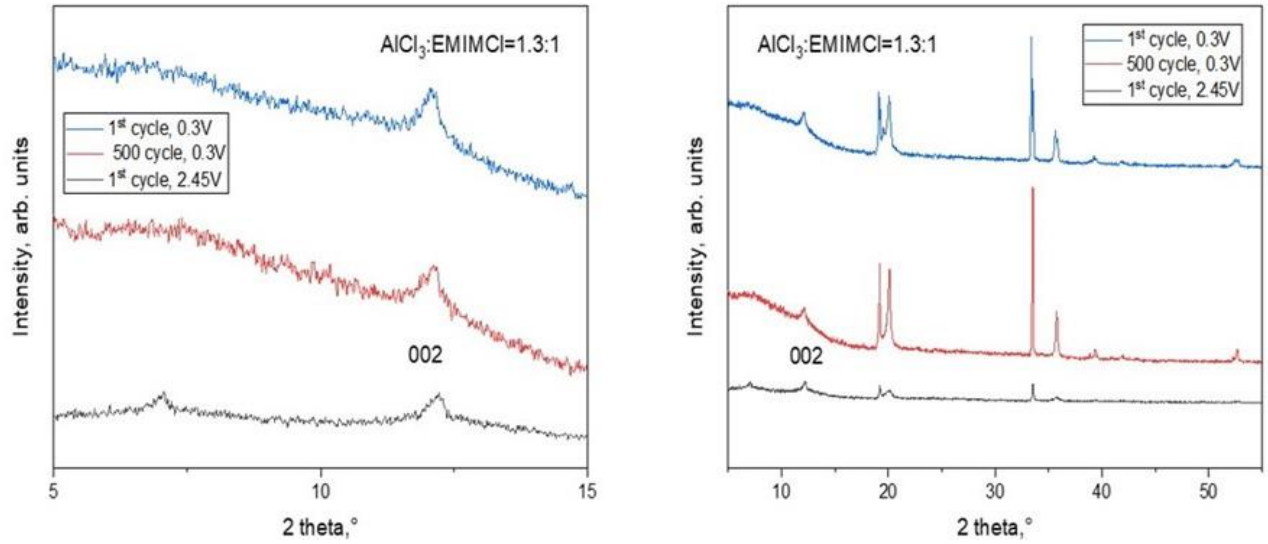
To’rtinchi bob “Grafen qog‘ozining Post mortem tahlili”

4.1-rasmda turli tayyorlash sharoitlarida olingan yangi grafit katodining eks-situ XRD spektrlari keltirilgan bo‘lib, ular materialning xos kristallik xususiyatlarini namoyon etadi. Barcha holatlarda (002) aks ettirish (refleksiya) taxminan 12° (2θ, Mo Kα) da kuzatiladi, bu esa qatlamlararo masofa taxminan 3.35 Å ga teng bo‘lib, c-o‘q bo‘ylab yaxshi tartiblangan grafit tuzilishini ko‘rsatadi. Qo‘shimcha ravishda, (100), (101), (110) va (112) kabi tekislik bo‘yicha aks ettirishlar mavjud bo‘lib, bu geksagonal tartib va yuqori kristallik darajasini tasdiqlaydi. (002) cho‘qqisining tor va simmetrik shakli tuzilmaviy buzilish yoki turbostratik beqarorlikning yo‘qligini anglatadi. Skan qilingan butun diapazonda past burchakli yoki tashqi fazaga tegishli aks ettirishlar aniqlanmagan, bu esa materialning strukturaviy sofligi va tayyorlangan elektrodda interkalyatsiya qilingan yoki oksidlangan turlar mavjud emasligini tasdiqlaydi..



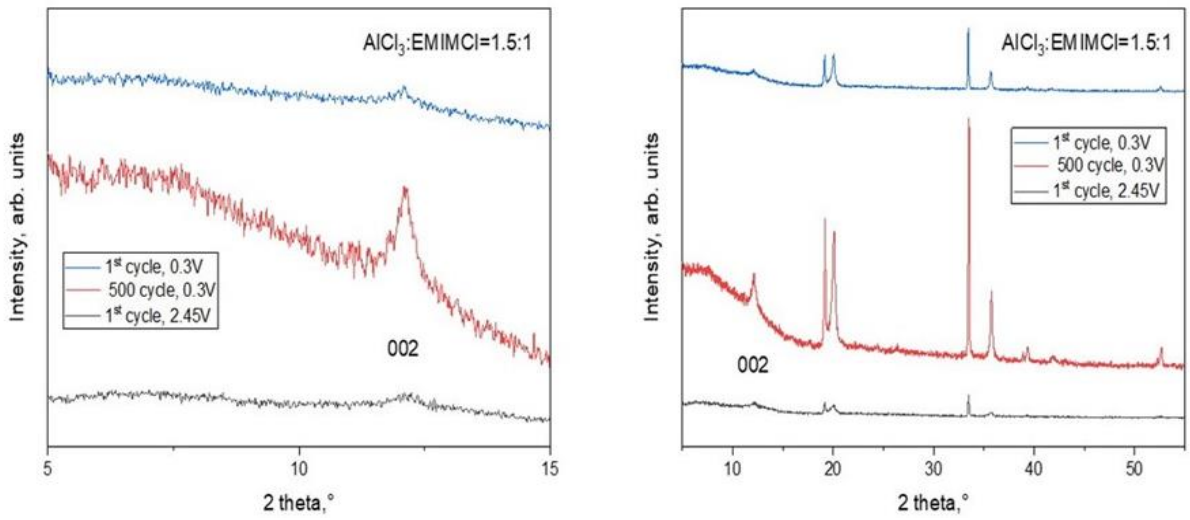
4.1-rasm. Yacheyka yig‘ilishidan oldingi grafen qog‘ozi va grafit elektrodlarining XRD tasvirlari

4.2-rasmda $AlCl_3$:[EMImCl] = 1.3:1 elektroliti uchun olingan eks-situ XRD spektrlari ikki xil 2θ diapazonida taqdim etilgan: past burchakli sohada (5–15°) grafitning (002) aks ettirishining evolyutsiyasi ko‘rsatilgan bo‘lsa, keng burchakli diapazonda (10–55°) elektrolitdan kelib chiqqan qo‘shimcha kuchsiz va keng aks ettirishlar namoyon bo‘ladi. 500 sikldan keyin (002) cho‘qqisi hali ham aniqlanadi, ammo u sezilarli darajada kengaygan va diffuz fonning oshishi bilan tavsiflanadi. Bu holat mikrotanaqish (microstrain), turbostratik buzilish va karbon tuzilmasining qisman amorflanishi rivojlanganini anglatadi, ayniqsa past kislotalik sharoitida. Eng muhim jihati shundaki, skan qilingan butun diapazonda yangi kuchli Bragg aks ettirishlari paydo bo‘lmagan, bu esa sikllash jarayonida tuzilmaviy beqarorlik oshganiga qaramasdan, ommaviy kristallik parchalanish mahsulotlari hosil bo‘lmaganini tasdiqlaydi.



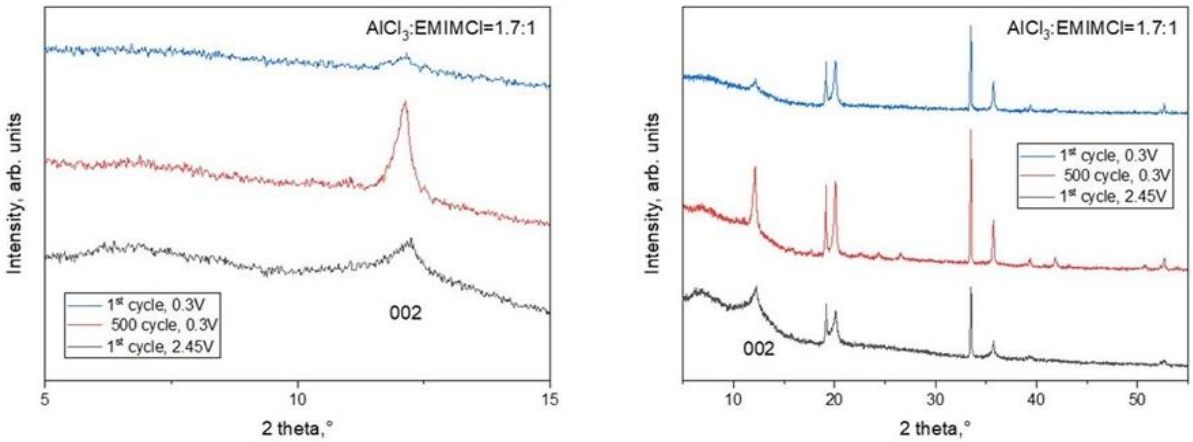
4.2-rasm. 1.3:1 Elektrolitda boshlang‘ich va uzoq muddatli sikllardan keyingi XRD tasvirlari

4.3-rasmda $AlCl_3$:[EMImCl] = 1.5:1 elektroliti 1.3:1 tizimiga nisbatan ancha qaytaruvchan (002) javobni namoyon etadi. Qayta zaryadlanish jarayonida (002) aks ettirishi o‘zining dastlabki sof holatidagi pozitsiyasiga yaqinlashadi, uning yarim balandlikdagi to‘liq kengligi (FWHM) torroq va diffuz fon pastroq bo‘ladi. Bu holat grafit qatlamlari ichidagi turbostratik buzilish va mikrotanaqishning kamayganini anglatadi. Keng burchakli diapazonda (10–55°) elektrolitdan kelib chiqqan mahsulotlarga tegishli bo‘lgan qoldiq keng aks ettirishlar ancha kuchsiz va sikllar davomida kamroq barqarorlikni namoyon etadi. Yangi o‘tkir Bragg aks ettirishlarining yo‘qligi interfeysning strukturaviy barqarorligini hamda o‘rta darajali Lyuis kislotalik sharoitida yondosh mahsulotlar to‘planishi kamligini tasdiqlaydi.



4.3-rasm. 1.5:1 Elektrolitda boshlang‘ich va uzoq muddatli sikllardan keyingi XRD tasvirlari

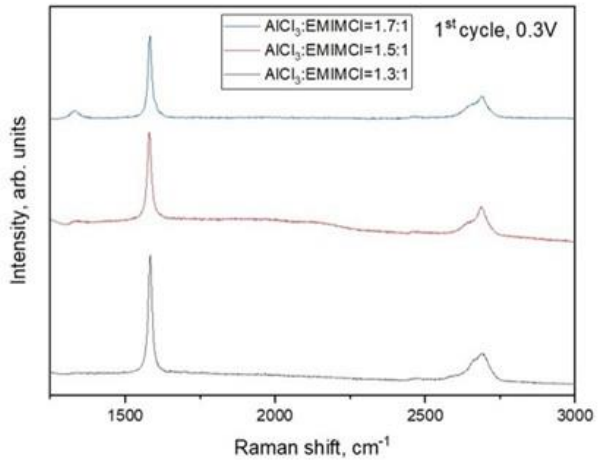
4.4-rasmda $AlCl_3$:[EMImCl] = 1.7:1 elektroliti sinovdan o‘tkazilgan tarkiblar ichida eng o‘tkir va eng qaytaruvchan grafit (002) javobini namoyon etadi. (002) cho‘qqisi eng tor yarim balandlikdagi to‘liq kenglikka (FWHM) ega bo‘lib, interkalyatsiya va deinterkalyatsiya jarayonlarida aniq va qayta takrorlanadigan siljishni ko‘rsatadi hamda minimal qoldiq kengayish bilan deyarli o‘zining sof holatidagi pozitsiyasiga qaytadi. 500 sikldan keyin ham past burchakli va keng burchakli diapazonlarda diffuz fon past darajada saqlanadi va deyarli hech qanday barqaror qo‘shimcha aks ettirishlar aniqlanmaydi. Bu esa toza va barqaror interfeys, shuningdek, kristallik yondosh mahsulotlarining yo‘qligini tasdiqlaydi. Ushbu natijalar yuqori Lyuis kislotalik sharoitida grafit katodida strukturaviy qaytaruvchanlikning yaxshilanishi, buzilish darajasining kamayishi va faza tozaligining oshishini aniq ko‘rsatadi.



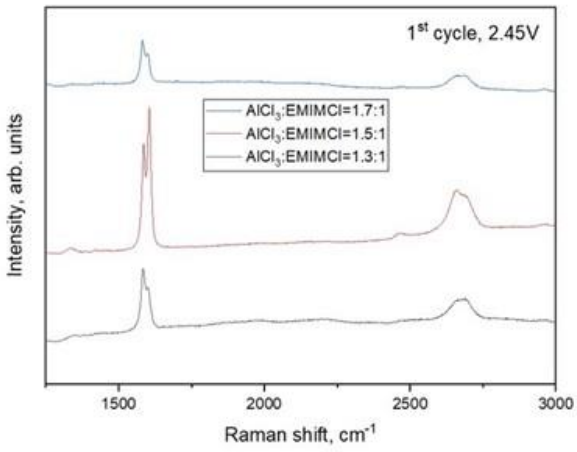
4.4-rasm. 1.7:1 Elektrolitda boshlang‘ich va uzoq muddatli sikllardan keyingi XRD tasvirlari

4.5-rasmda $AlCl_3$:[EMImCl] elektrolitining Lyuis kislotaligi ortib borishi (1.3:1 → 1.5:1 → 1.7:1) bilan 0.3 V (birinchi razryad) da yozib olingan Raman spektrlari tizimli p-tip doping tendensiyasini namoyon etadi. $AlCl_3$ miqdori oshgan sari G-

band yuqori chastota tomon siljiydi va biroz torlaydi, 2D-band esa kuchsizlanadi, kengayadi va ozgina past chastotaga siljiydi, shu bilan birga ID/IG intensivlik nisbati past bo‘lib qoladi, ammo ozgina o‘sish ko‘rsatadi. Bu bir vaqtda kechuvchi siljishlar anion–π zaryad almashinuvi va bosqichlanish (staging) jarayonlarining kuchayganini anglatadi, bu esa yuqori kislotalikda $AlCl_4^-$ ionlari bilan grafit qatlamlari o‘rtasidagi elektron o‘zaro ta’sirning kuchayishi bilan muvofiq keladi. Shu bilan birga, ID/IG nisbatining past va barqaror saqlanishi bu o‘zaro ta’sir reshyotkaga jiddiy shikast yetkazmasdan amalga oshishini, ya’ni samarali p-doping va grafit tuzilmasining yaxlitligini saqlashini tasdiqlaydi.



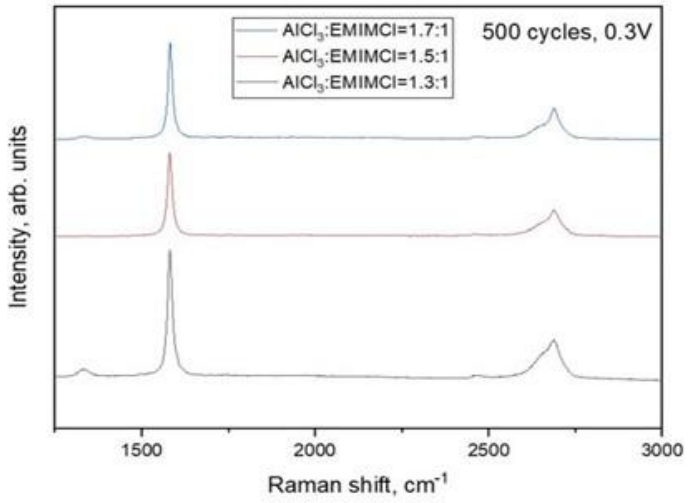
4.5-rasm. Grafen qog‘ozi va turli molyar nisbatdagi elektrolitlarning birinchi sikldagi (0.3 V) Raman tahlili



4.6-rasm. Grafen qog‘ozi va turli molyar nisbatdagi elektrolitlarning birinchi sikldagi (2.45 V) Raman tahlili

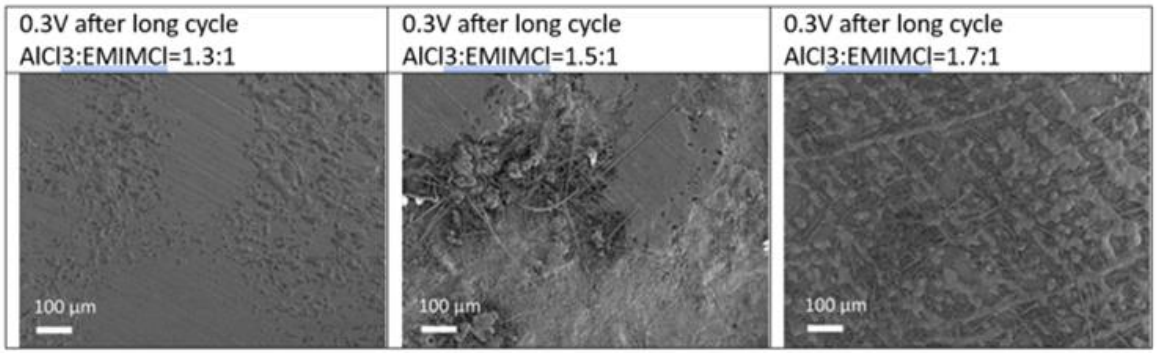
4.6-rasmda 2.45 V (birinchi zaryad) da yozib olingan Raman spektrlarida G-bandning aniq yuqori chastotaga siljishi va ikkiga bo‘linishi kuzatiladi, bu esa zaryadlangan va zaryadlanmagan grafit tekisliklariga mos keladi. Shu bilan bir vaqtda 2D-band keskin kuchsizlanadi va sezilarli darajada kengayadi, bu esa qabul qiluvchi (acceptor-type) bosqichlanish hamda $AlCl_4^-$ interkalyatsiyasi natijasida hosil bo‘lgan kuchli π-zona (π-band) teshik-dopingning xos belgilari hisoblanadi. Bu ta’sirlar 1.7:1 elektrolit eritmasida eng kuchli namoyon bo‘lib, yuqori kislotalik sharoitida chuqurroq va yaxshiroq tartiblangan bosqichlanish hamda kuchaygan zaryad almashinuvni anglatadi. Shu bilan birga, ID/IG nisbati deyarli o‘zgarishsiz qoladi, bu esa ushbu kuchli elektron o‘zaro ta’sir yangi nuqsonlar hosil qilmasdan amalga oshishini ko‘rsatadi. Raman natijalari XRD kuzatuvlari bilan to‘liq mos keladi, chunki 1.7:1 tizimida ham (002) aks ettirish eng o‘tkir va eng qaytaruvchan ko‘rinishni namoyon etgan. Bu esa interkalyatsiya–deinterkalyatsiya jarayonlarining strukturaviy yaxlit va muvofiq tarzda kechishini tasdiqlaydi. 4.7-rasmda 0.3 V da (500 sikldan keyin) yozib olingan Raman spektrlari keltirilgan bo‘lib, G-band o‘zining sof holatidagi pozitsiyasiga qaytib yaqinlashgani kuzatiladi. Shu bilan birga, I_D/I_G nisbati barqaror ravishda past darajada saqlanadi, ayniqsa 1.7:1 elektroliti uchun bu holat yaqqol ko‘rinadi. Bu esa doimiy tarkibiy buzilish minimal

ekanligini va $AlCl_4^-$ ionlarining chiqib ketishi (deinterkalyatsiya) bilan p-dopingning qisman qaytganini anglatadi. 2D-band hamon aniq kuzatiladi, faqat ozgina kengayish bilan, va hech qanday yangi nuqsonlar bilan bog‘liq bandlar paydo bo‘lmagan. Ushbu natijalar grafit tuzilmasining kristall tartibi saqlanib qolganini, hamda uzoq sikllardan keyin ham ximiyaviy jihatdan barqaror interfeys hosil bo‘lganini tasdiqlaydi. Shu bilan birga, bu ma’lumotlar yuqori Lyuis kislotalik sharoitida grafit katodining strukturaviy chidamliligi va barqarorligini yaqqol namoyon etadi.

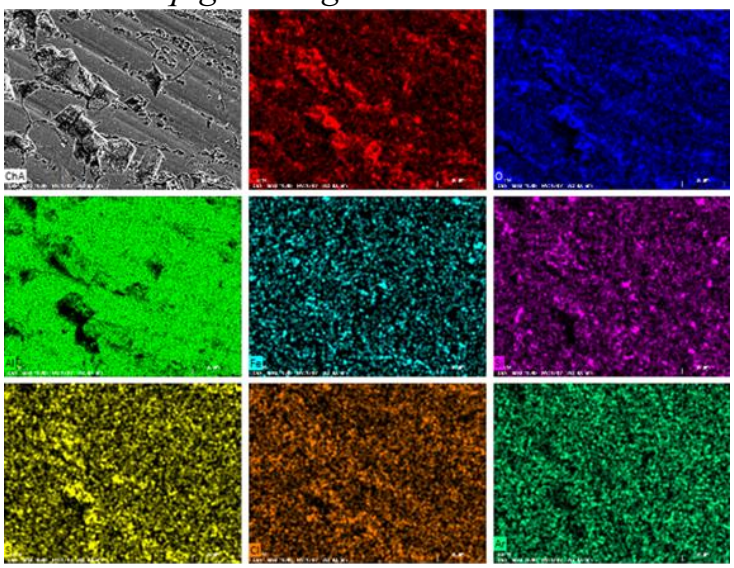


4.7-rasm. Grafen qog‘ozi va turli molyar nisbatdagi elektrolitlarning 500 ta sikldan keyingi Raman tahlili

4.8-rasmda 0.3 V gacha uzoq sikldan keyingi grafit katodiga oid eks-situ SEM tasvirlari keltirilgan bo‘lib, ular elektrolit kislotaligiga bog‘liq holda yuza morfologiyasining yaqqol farqlanishini ko‘rsatadi. 1.3:1 elektrolitda elektrod yuzasi qisman elektrolit qoldiqlariga xos uzluksiz bo‘lmagan, plyonkasimon qatlamlar bilan qoplangan. 1.5:1 nisbatda yuza tuzilishi yanada qovuroq va noxomogen ko‘rinishda bo‘lib, lokal o‘smalar va yopiq emas qoplamali uchastkalar kuzatiladi. Bunga qarshi ravishda, 1.7:1 elektrolitda grafitning qatlamli (lamellar) tuzilishi yaxshi saqlanib qoladi, qirralar ancha toza va aniq, hamda zarrachaviy chiqindilar miqdori keskin kamaygan. Yuza aniqligi va tozaligining bunday izchil yaxshilanishi Lyuis kislotalikning ortishi bilan bog‘liq bo‘lib, bu o‘z-o‘zini cheklovchi (self-limiting) barqaror interfeys qatlamining hosil bo‘lishi va 1.7:1 tizimida yondosh parazit qoplanish jarayonlarining susayganini ko‘rsatadi.



4.8-rasm. Turli molyar nisbatdagi elektrolitlarning uzoq sikldan keyingi grafen qog‘ozining SEM tasvirlari



Element	Atomic No.	Net Counts	Mass %	Mass % (Norm.)	Atoms %	Abs. Error (Mass%)	Rel. Error (%)
Carbon	6	22 556	5.95	10.50	20.74	±0.31	5.25
Oxygen	8	20 584	1.30	2.29	3.39	±0.05	4.13
Aluminium	13	2 206 803	48.33	85.27	74.97	±1.41	2.92
Argon	18	2 065	0.16	0.27	0.16	±0.01	7.46
Iron	26	1 412	0.88	1.55	0.66	±0.07	8.34
Silicon	14	0	0.00	0.00	0.00	0.00	999.00
Sulfur	16	0	0.00	0.00	0.00	0.00	999.00
Chlorine	17	1 205	0.07	0.12	0.08	±0.01	11.88
Sum			56.68	100.00	100.00		

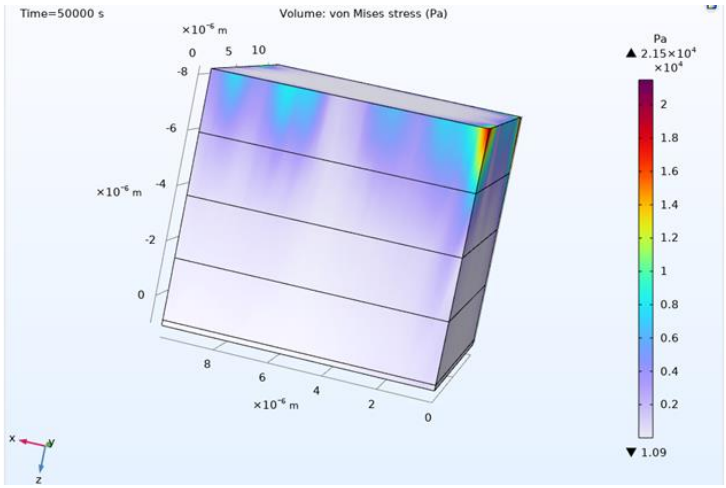
4.9-rasm. Uzoq sikldan keyingi grafen qog‘ozining SEM va EDS tahlillari

4.9-rasmda keltirilgan SEM–EDS tahlil natijalari grafit katodi yuzasidagi elementlar taqsimotining bir xilligini namoyon etadi. (a)-rasmdagi EDS xaritalarida C, O, Al va Cl elementlari bir teks taqsimlangan bo‘lib, lokal konsentratsiya nuqtalari yoki “hotspotlar” aniqlanmagan. Bu holat kristallik tuzilmali tuzlar yoki metall klasterlar yo‘qligini hamda bir jinsli, yupqa CEI (katod elektród interfeysi) qatlamining hosil bo‘lganini ko‘rsatadi. (b)-rasmdagi tegishli EDS spektrlari asosan karbon signali bilan hukmron bo‘lib, unda faqat kichik miqdorda Al va iz miqdorda Cl/O belgilar kuzatiladi. Bu natija nanomiqyosdagi CEI qatlami tarkibida qoldiq xlor-alyuminat va okso-komponentlar mavjudligini ko‘rsatadi. Umuman, ushbu natijalar bir jinsli va kimyoviy jihatdan yupqa interfeys qatlamining hosil bo‘lishini, kristallik yondosh tuzilmalar emas, balki barqaror amorf CEI shakllanishini tasdiqlaydi.

Beshinchi bob “COMSOL Multifizik modellashtirish”

5.1-rasmda keltirilgan 3D COMSOL kimyo-mexanik simulyatsiyasi galvanostatik ishlash sharoitidagi laminatlangan grafen qog‘ozi elektrodida yuzaga keladigan ichki mexanik kuchlanishlarning taqsimotini ko‘rsatadi. Hisoblash natijalariga ko‘ra, fon Mizes (von Mises) stress konsentratsiyalari asosan qog‘ozning qirralarida, burchaklarida, qatlamlar tugash joylarida hamda tok kollektori bilan tutashgan interfeysda joylashadi, shu bilan birga ichki qatlamlar nisbatan tinch va past kuchlanish holatida saqlanadi. Bu mahalliy stress nuqtalari $AlCl_4^-$ ionlarining nomutanosib interkalyatsiyasi natijasida yuzaga keladi, chunki u laminat qalinligi bo‘ylab ichki deformatsiya (eigenstrain) gradiyentlarini hosil qiladi. Tok kollektorining mexanik cheklovi interkalyatsiyadan kelib chiqqan kengayish nomutanosibligini mahalliy siljish va egilish stresslariga aylantiradi, natijada interfeysda stress to‘planishi kuzatiladi.

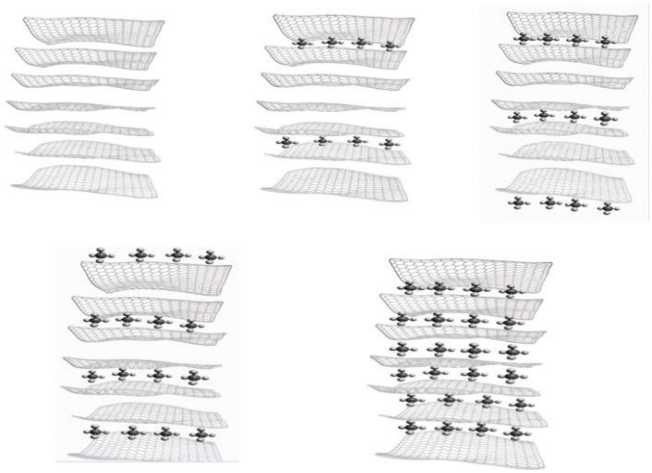
Simulyatsiya natijalari shuni ko‘rsatadiki, grafen qog‘ozi elektrodlaridagi stress yig‘ilishini kamaytirish va interfeys degradatsiyasini oldini olish uchun bir qator dizayn optimallashtirish choralari samarali bo‘lishi mumkin. Ular qatoriga elastik va ion o‘tkazuvchan oraliq qatlamlar joriy etish, qirra geometriyasini yumshatish yoki aylanasimon shaklga keltirish, tokni bir tekis tarqatuvchi kollektor tizimlarini qo‘llash, shuningdek g‘ovaklik yoki elektr o‘tkazuvchanlik bo‘yicha gradiyentli tuzilishlarni muhandislik yo‘li bilan yaratish kiradi. Ushbu yechimlar stress to‘planishini kamaytiradi va elektrodning uzoq muddatli mexanik barqarorligini ta’minlaydi.



5.1-rasm. Galvanostatik ish rejimida grafen qog‘ozidagi von Mises kuchlanish taqsimotining COMSOL simulyatsiyasi

5.2-rasmda Ryudorff–Hofmann modeli asosidagi sxema grafen qatlamlaridagi $AlCl_4^-$ ionlarining diskret bosqichma-bosqich qatlamlanishini (staging) tasvirlaydi. Bu jarayon kam interkalyatsiya holatidan zich interkalyatsiya holatigacha bo‘lgan

o‘tishni ifodalaydi. Har bir bosqichda COMSOL modelini qurish uchun $\varepsilon^*(\theta) = \alpha\_c(\theta) e\_c \otimes e\_c$ ko‘rinishidagi xususiy deformatsiya (eigenstrain) qo‘llaniladi, bunda θ_n — qoplanish darajasi, $\alpha\_c(\theta_n)$ esa c-o‘qi bo‘ylab kengayish koeffitsiyenti sifatida belgilangan. Interkalyatsiyaning ilk bosqichlari asosan qirra hududlarida shakllanadi, natijada θ gradiyenti ($\nabla\theta$) katta bo‘ladi va mahalliy kuchlanishlar konsentratsiyasi yuzaga keladi. Keyingi, yuqori bosqichlarda interkalyatsiya bir tekis tarqaladi, ammo bu holat umumiy deformatsiya energiyasining ortishiga olib keladi. Ushbu qatlamlanish modeli elektrokimyoviy ma’lumotlar — CV cho‘qqilari, XRD (002) cho‘qqilarining siljishi va Raman spektrlaridagi o‘zgarishlar — bilan bog‘lanadi va ularni konstitutiv kirish parametrlari sifatida ($\alpha\_c(\theta)$, $i_0(\theta)$, $D(\theta)$) foydalanish imkonini yaratadi. Shu orqali, ko‘p qatlamli grafen qog‘ozi elektrodlari uchun prognostik kimyo-mexanik simulyatsiyalarni amalga oshirish imkoni vujudga keladi.



5.2-Rasm. Grafen qog‘ozida $AlCl_4^-$ interkalyatsiyasining qatlamlanish sxemasi

XULOSA

1. Tadqiqot natijalari elektrod strukturasi va elektrolitning $AlCl_3$:[EMIm]Cl nisbati ADIA tizimining funksional samaradorligini belgilovchi asosiy omillar ekanini ko‘rsatdi. Bindersiz grafen qog‘ozning yuqori o‘tkazuvchan arxitekturali ion transportining jadallashuvi hamda $AlCl_4^-$ interkalatsiyasining yuqori qaytariluvchanligi ta’minlab, grafit kompozitiga nisbatan yaxshiroq natija qayd etdi. Sinovlar orasida 1.7:1 molyar nisbatli elektrolit eng barqaror uzoq muddatli sikllanishni ko‘rsatdi, 1.5:1 tizimi esa faqatgina ayrim boshlang‘ich zaryard-razryad jarayonalarida yuqori ko’rsatkichlarni namoyon qildi. Ushbu farqlar ADIA yacheykalarida ion harakatchanligi, Lyuis kislotaligi va qatlamlararo barqarorlikning murakkab ammo o‘zaro bog’liqligini tasdiqlaydi.

2. Swagelok-tipidagi Al/grafen va Al/grafit yacheykalari CV, EIS va GCPL sinovlari orqali baholandi. 25 mA· g^{-1} tok zichligida grafit taxminan 90 mAh · g^{-1}, grafen qog‘ozi esa 80 mAh· g^{-1} atrofidagi sig‘imni ko‘rsatdi; biroq yuqori tok zichliklarida grafen qog‘ozi ion va elektron transport hususiyatlarini hisobiga, yaxshiroq natija ko’rsatdi. 100 mA· g^{-1} tok zichligidagi sikllanish vaqtida grafen qog‘oz 500 sikldan so‘ng 70–75 mAh· g^{-1} atrofida barqarorlashdi va deyarli 100 % Kulon effektevligini namoyish qildi. COMSOL modellashtirish natijalari ~2×10^4 Pa maksimal von Mises stressini ko‘rsatdi, bu esa faqat juda kichik miqdorda deformatsiya yuz berishini va bindersiz grafen qog‘ozning yuqori mexanik barqarorligini tasdiqlaydi.

3. Turli $AlCl_3$:[EMIm]Cl nisbatlarida (1.3:1, 1.5:1, 1.7:1) zaryadlash (2.45 V) va razryadlash (0.3 V) jarayonlaridan so‘ng, 1 va 500-sikllarda olingan bindersiz grafen qog‘ozi katodining XRD spektrlari aniq strukturaviy farqlarni ko‘rsatdi. MoKα nurlanishida 12° atrofida kuzatilgan keng (002) cho‘qqi grafen qog‘ozning turbostrukturali tabiatini tasdiqladi. 500 sikldan so‘ng 1.7:1 tizimi aniq (002) cho‘qqisini saqlab qoldi va bu katod materialini elektrokimyoviy barqarorligini ko‘rsatadi.

4. Turli $AlCl_3$:[EMIm]Cl nisbatlarida (1.3:1, 1.5:1, 1.7:1) olingan bindersiz grafen qog‘ozning ex-situ Raman spektrlari sp^2-uglerodga xos xususiyatlarini namoyon etdi. 2.45 V gacha zaryadlash jarayonida G-tasmaning biroz siljishi va ID/IG nisbatining oshishi $AlCl_4^-$ interkalatsiyasi natijasida yuzaga kelgan qaytariluvchi panjara stressini ko‘rsatdi. 500 sikldan so‘ng, 1.7:1 nisbatli elektrolit Raman tasmalarining deyarli o‘zgarmasligini saqlab qoldi, bu esa uning strukturaviy barqarorligini tasdiqladi. Aksincha, 1.3:1 va 1.5:1 tarkiblarda D-tasmaning kuchayishi ko‘zga tashlanib, bu sikllanish davomida nuqsonlarning to‘planishi bilan bog‘landi. Ushbu natijalar yuqori Lyuis kislotaligi (1.7:1) yanada barqaror interkalatsiya va panjara yaxlitligini saqlashga yordam berishini ko‘rsatadi.

5. Optimallashtirilgan 1.7:1 $AlCl_3$:[EMIm]Cl elektrolit va paketli geomteriyaga ega Al/grafen yacheyka o‘rtacha darajadagi tok zichligiga chidamlilik va yaxshi sikl qaytuvchanlikni namoyish etdi. Yacheyka 11 mA· g^{-1} tok zichligida taxminan 95 mAh· g^{-1} sig‘im berdi va 95 % Kulon effektevligini ham saqlab qoldi. Biroq yuqori tok zichliklarida sig‘imning bosqichma-bosqich kamayishi kuzatilib, bu tezkor ishlash sharoitida $AlCl_4^-$ ionlarining sust diffuziyasi hamda elektrolit viskozligining ortishi bilan bog‘liq tok zichligiga chidamlilikni qisman buzilishini ko‘rsatdi. Uzoq sikllik test davomida yacheyka 160 sikl oralig’ida barqarorlikni saqlab qola oldi. Shunga qaramay, amaliy ADIA tizimlari uchun uzoq muddatli barqarorlik va energiya samaradorligini oshirish maqsadida elektrolit tarkibini va katod arxitekturasini yanada optimallashtirish zarur bo’ladi.

SCIENTIFIC COUNCIL ON AWARDING OF SCIENTIFIC DEGREES DSc.02/30.12.2019.FM/T.65.01 INSTITUTE OF ION-PLASMA AND LASER TECHNOLOGIES

INSTITUTE OF ION-PLASMA AND LASER TECHNOLOGIES

ASHUROV ILKHOMJON KHATAM UGLI

EXPERIMENTAL INVESTIGATION AND COMPUTATIONAL MODELING OF GRAPHENE CATHODES AND ROOM-TEMPERATURE IONIC-LIQUID ELECTROLYTES FOR ALUMINUM BATTERIES

01.04.12 – Physics and technology of nanomaterials

ABSTRACT
of dissertation of the doctor of Philosophy (PhD)
on physical and mathematical sciences

TASHKENT – 2025

The theme of the dissertation of doctor of philosophy (PhD) on physical and mathematical sciences was registered at the Supreme Attestation Commission of the Ministry of Higher Education, Science and Innovation of the Republic of Uzbekistan under № B2025.3.PhD/FM1385

Dissertation has been prepared at the Institute of Ion-plasma and laser technologies.

The abstract of the dissertation in three languages (Uzbek, Russian, English (resume)) has been posted on the website of the Scientific Council (www.iplt.uz) and on Information-educational portal «ZiyoNet» (http://www.ziyonet.uz).

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Leading organization:	**Tashkent State Technical University named after Islam Karimov**

The defense will take place on «11» december 2025 at 14:30 at the meeting of the Scientific Council number DSc.02/30.12.2019.FM/T.65.01 at Institute of Ion-Plasma and Laser Technologies (Address: 100125, Uzbekistan, Tashkent, 33 Durmon yuli street. Phone/fax: (+99871) 262-32-54, e-mail: info@iplt.uz).

The PhD dissertation is can be looked through in the Information-Resource Centre of the Institute of Ion-Plasma and Laser Technologies (is registered № 21) (Address: 100125, 33, Durmon yuli str., Tashkent, Uzbekistan. Phone: (+99871) 262-31-69).

The abstract of the dissertation is sent out on «02» december 2025.

(Mailing report № 21on «02» december 2025).

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INTRODUCTION (PhD Dissertation Abstract)

Relevance and significance of the dissertation topic: In recent decades, the rapid global shift toward renewable energy integration, electrified transportation, and sustainable material cycles has intensified the need for advanced electrochemical energy storage systems. Modern applications in electric mobility, grid stabilization, portable electronics, and environmental monitoring demand batteries that combine high performance, operational safety, long service life, and the use of earth-abundant elements. Meeting these requirements, calls for the continuous development of novel electrode materials, optimized electrolytes, and advanced characterization and modeling approaches.

Among emerging post-lithium chemistries, aluminum dual-ion batteries (ADIB) have attracted growing attention as a sustainable and cost-effective alternative. Aluminum is the most abundant metallic element in the Earth's crust and offers multiple advantages — low cost, non-toxicity, high volumetric capacity, and excellent recyclability — making it an ideal candidate for next-generation energy storage. In Lewis-acidic $AlCl_3$–1-ethyl-3-methylimidazolium chloride [EMImCl] electrolytes, ADIB operate through a dual-ion electrochemical mechanism, in which metallic aluminum is reversibly deposited and stripped at the anode via the $Al_2Cl_7^-$/Al redox couple, while complex chloroaluminate anions ($AlCl_4^-$) are intercalated and de-intercalated within layered sp^2-carbon frameworks at the cathode. Within this system, graphite and binder-free graphene paper stand out as highly promising cathode materials. Their excellent electrical conductivity, structural order, and mechanical flexibility enable rapid ion–electron transport and reversible interlayer expansion during the staging of $AlCl_4^-$ anions. In particular, binder-free graphene paper offers a lightweight, current-collector-free, and highly conductive architecture with short diffusion paths, abundant edge and defect sites, and strong mechanical integrity, leading to improved rate capability, reduced polarization, and extended cycling stability compared with conventional graphite electrodes.

The overall performance of ADIB is governed by multiple interdependent factors, including electrolyte speciation (controlled by the $AlCl_3$:[EMImCl] molar ratio), cathode microstructure (porosity, thickness, interlayer spacing, and tortuosity), and interfacial chemistry at the cathode–electrolyte boundary. Therefore, a systematic investigation combining experimental and computational methods is essential to elucidate the relationships between electrolyte composition, electrode architecture, and interfacial dynamics. Such a comprehensive understanding provides the scientific foundation for the rational design of high-efficiency, durable, and scalable ADIB that meet the growing global demand for sustainable and safe electrochemical energy storage.

This research contributes to the implementation of the tasks outlined in the Decree of the President of the Republic of Uzbekistan No. PF-60 dated January 28, 2022, "On the Strategy for the Development of New Uzbekistan in 2022–2026", the Decree No. PF-2789 dated February 17, 2017, "On Further Improvement of the Activities of the Academy of Sciences, Organization, Management, and Financing

of Scientific Research", and the Decree No. PF-4422 dated August 22, 2019, "On Urgent Measures to Increase Energy Efficiency in the Economy and Special Sectors, Implement Energy-Saving Technologies, and Develop Renewable Energy Sources."

Relevance of the research to the priority areas of scientific and technological development of the republic: This research is fully consistent with the strategic priorities of the Republic of Uzbekistan in the areas of energy efficiency, renewable energy integration, and advanced materials science. It contributes to the national objectives of sustainable technological development by advancing safe, durable, and manufacturable electrochemical energy storage systems that facilitate the transition toward a low-carbon and resource-efficient economy.

State of the art of the problem: Globally, aluminum-based dual-ion and aluminium-ion battery research is actively pursued by leading academic groups and commercial ventures. The Hongjie Dai group (Stanford University / SLAC) pioneered high-rate aluminum–graphite cells and operando Raman studies on chloroaluminate intercalation. The Helmholtz Institute Ulm / Karlsruhe Institute of Technology (KIT) together with partner institutions have executed operando XRD, tomography, and modeling workflows to analyze staging and degradation of carbon hosts.

The University of Queensland (UQ) / Graphene Manufacturing Group (GMG) collaboration is among the few pushing toward commercialization, working on graphene aluminum-ion battery prototypes and partnering with the Battery Innovation Center (Indiana, USA). In Europe, Albufera Energy Storage (Spain) is developing aluminum-ion cell prototypes and promoting scaling routes for sustainable battery manufacturing. Several research groups in Germany, Switzerland (e.g. Empa), and France are actively exploring advanced carbon cathodes and ionic liquids, often coupling in-situ/operando spectroscopy with continuum modeling. At the materials frontier, recent work by Ursula Krossing's group (University of Freiburg / Ulm) introduced organic redox polymer cathodes for Al-ion contexts, demonstrating extended cycling in alternative cathode chemistries. In addition, TasmanIon, co-founded by researcher linked to the MacDiarmid Institute (New Zealand / Australia), is attempting to commercialize aluminium-ion battery technology developed in academia.

Despite these achievements, the majority of studies to date remain compartmentalized—focusing on electrolyte speciation, carbon architectures, or operando techniques separately. Few groups have integrated all three dimensions (electrochemical performance, structural dynamics, and computational modeling) into a unified, cross-validated framework—especially for aluminum dual-ion systems involving sp^2-carbon cathodes. This gap motivates the comprehensive, mechanism-driven, cross-disciplinary approach of the present work.

Connection of the dissertation research with the scientific projects of the research institute: The dissertation was carried out at the Institute of Ion-plasma and laser technologies of the Academy of Sciences of the Republic of Uzbekistan in accordance with its fundamental research program on nanostructured materials and advanced electrochemical systems. The project complements ongoing national and

international collaborations in the fields of energy storage materials, modeling of intercalation mechanisms, and sustainable energy technologies. This research was supported by the grant No. AL-5921122118 of the Agency for Innovative Development of the Ministry of Higher Education, Science and Innovation of the Republic of Uzbekistan.

Aim of the research: The aim of this research is to develop a mechanistic framework for the optimization of ADIB through an integrated study of electrolyte acidity and speciation, carbon-cathode architecture, and cathode–electrolyte interfacial stability. The work combines advanced electrochemical diagnostics, structural and interfacial characterization, and multiphysics computational modeling to establish comprehensive design principles for high-performance and durable ADIB systems.

Research objectives:

- to prepare binder-free graphene paper and graphite composite cathodes, compare their electrochemical characteristics, and analyze the intercalation mechanism to identify the most optimal electrode material for aluminum batteries;
- to prepare $AlCl_3$:[EMIm]Cl–based ionic-liquid electrolytes with 1.3:1, 1.5:1, and 1.7:1 molar ratios, and to optimize electrolyte properties by controlling Lewis acidity and ionic speciation;
- to assemble Al/graphene and Al/graphite cells in both Swagelok and pouch-cell geometries, and evaluate their performance using CV (cyclic voltammetry), EIS (electrochemical impedance spectroscopy), and GCPL (galvanostatic cycling with potential limitation);
- to investigate the $AlCl_4^-$ intercalation mechanism using ex-situ XRD by tracking interlayer spacing expansion and the formation of well-defined staging during repeated charge–discharge processes;
- to analyze structural and mechanical changes using ex-situ Raman spectroscopy, and to assess stress generated by interlayer expansion; additionally, to model these effects using COMSOL Multiphysics;
- based on the optimized performance of Swagelok-type ADIB cells, to design pouch-cell prototypes and integrate the results into a comprehensive electrochemical evaluation;

Object of the research: $AlCl_3$:[EMImCl] ionic liquid electrolytes, graphite and binder-free graphene-paper cathodes, laboratory-scale aluminum dual-ion cells including Swagelok and pouch cells.

Subject of research: The electrochemical intercalation and staging processes of $AlCl_4^-$ in carbon cathodes, their relationship with electrolyte speciation and interfacial chemistry, porous electrode transport, and intercalation-induced strain.

Research methods: Electrochemical methods - Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge–discharge (GCPL) measurements were performed under standardized conditions with iR-compensation and current normalization to evaluate kinetic behavior, charge-transfer resistance, and reversibility. Structural and surface characterization - X-ray diffraction (XRD) in reflection, capillary, and grazing-incidence modes, Raman

spectroscopy, and scanning electron microscopy with energy-dispersive spectroscopy (SEM/EDS) were employed to examine phase composition, lattice parameters, morphology, and elemental distribution. Computational modeling - Multiphysics simulations were conducted in COMSOL Multiphysics to model electrolyte diffusion, intercalation-induced strain, and stress evolution within graphene-paper laminates.

Scientific novelty of the research:

- for the first time, a commercially available binder-free graphene paper was employed as a cathode material in ADIBs, eliminating the electrochemically inactive components and avoiding the complex multistep fabrication procedures typical of conventional electrodes;
- for the first time, binder-free graphene paper and graphite-composite cathode materials were systematically evaluated electrochemically in room-temperature ionic-liquid electrolytes with various $AlCl_3$:[EMIm]Cl molar ratios. This comprehensive analysis revealed the fundamental закономерности of electrode–electrolyte interactions and identified the optimal electrolyte composition ensuring maximum cell performance;
- for the first time, ex-situ XRD and Raman spectroscopy results were integrated with computations from the Solid Mechanics module in COMSOL Multiphysics, enabling a precise assessment of structural changes and mechanically induced stresses developing within the cathode architecture during charge–discharge cycling. This integrated approach provided a deep, multi-factor understanding of the mechanical and electrochemical stability of the electrode material;
- for the first time, the development of an optimized cell structure—guided jointly by modeling outputs and experimental observations—demonstrated a critical scientific step toward creating pouch-type ADIB cells that combine mechanical flexibility with high electrochemical efficiency.

Practical results of the research: Standardized laboratory protocols for ADIB have been developed using both Swagelok and pouch-type cell configurations, ensuring reproducible assembly, reliable testing, and consistent electrochemical evaluation across all experimental stages. Architectural design guidelines for binder-free graphene-paper cathodes have been formulated to mitigate ionic and structural bottlenecks identified during experimentation. These guidelines enhance ion-transport uniformity, mechanical integrity, and electrochemical accessibility throughout multilayer graphene laminates, providing a foundation for reproducible and scalable electrode fabrication. Scale-up acceptance metrics have been established to facilitate the transition from fundamental Swagelok-cell measurements to laboratory-scale pouch-cell prototypes, thereby enabling systematic performance benchmarking and minimizing variability between test configurations. Electrolyte–cathode compatibility criteria have been defined for the $AlCl_3$:[EMImCl] system, identifying optimal compositions and carbon architectures under controlled laboratory conditions to ensure stable operation, reduced polarization, and extended cycle life in ADIB cells.

Reliability of the results: The reliability of the obtained results is ensured through systematic calibration against reference standards, replicate electrochemical measurements, and statistical confidence analysis of the experimental data. Structural and electrochemical findings were cross-validated to confirm internal consistency between XRD, Raman, SEM/EDS, CV, EIS, and GCPL results. The computational modeling was verified through mesh convergence tests, solution sensitivity analysis, and quantitative comparison with experimental observations, confirming the robustness and reproducibility of the developed framework.

Scientific and practical significance of the research results: The conducted research makes a substantial scientific contribution to the field of electrochemical energy storage by elucidating the coupled influence of electrolyte acidity, anionic speciation, and carbon-cathode architecture on the performance of ADIB. The integration of electrochemical diagnostics, structural characterization, and multiphysics modeling has enabled the formulation of a mechanistic framework describing ion staging, interfacial evolution, and chemo-mechanical behavior within binder-free graphene-paper electrodes. These outcomes extend the current understanding of multivalent ion intercalation dynamics and provide a generalized conceptual basis for designing advanced carbon-based energy-storage materials.

From a practical standpoint, the study establishes a coherent set of laboratory methodologies and optimization criteria for evaluating electrolyte–cathode systems under controlled conditions. The developed graphene-paper architecture guidelines and scaling metrics offer reproducible reference points for laboratory-scale ADIB assembly and performance benchmarking. Moreover, the COMSOL Multiphysics simulation framework, validated against experimental data, constitutes a transferable modeling tool for analyzing transport–mechanics coupling in a broad range of multivalent electrochemical systems.

Implementation of the research results:

Within the framework of the dissertation research, the scientific results obtained were successfully implemented in the project “Technical Regulation for Ensuring the Charge–Discharge Stability of Electroscooter Battery Modules, GCPL Diagnostics, and Extension of Service Life” (No. 27/10-2025), developed in cooperation with VV-LAND LLC. These solutions make it possible to determine the optimal state-of-charge window for the batteries (SoC 40–80%), enhance the stability of passive cell balancing, and enable early detection of degradation processes based on GCPL and EIS methods. The practical implementation of these scientific and technical developments has been confirmed by an official document provided by VV-LAND LLC.

The article dedicated to the current challenges, achievements, and future prospects of aluminum-ion batteries — “Current Challenges, Progress and Future Perspectives” (Applied Solar Energy, 2022, Vol. 58, No. 3, pp. 334–354. DOI: 10.3103/S0003701X22030033) — has been cited by international researchers in a number of publications, including J. Chai et al. (Energy Storage Materials, 81, 2025), H. Zhao et al. (Advanced Functional Materials, 2025), R. Afian et al. (Journal of the Physical Society of Indonesia, 1, 2025), A. Borozdin et al. (Russian

Metallurgy, 2, 2025), Y. Zhou et al. (Energy Technology, 13(4), 2024), and M. Saghir et al. (Applied Solar Energy, 60(3), 2024).

Approbation of the research results: The results of this research were presented and discussed at four international scientific and practical conferences, where they underwent approbation and received positive evaluation from the academic community.

Publication of the research results: A total of five scientific papers have been published based on the dissertation research. Among them, two papers were published in international scientific journals, and three papers were published in peer-reviewed journals of the Republic of Uzbekistan recommended by the Higher Attestation Commission of the Republic of Uzbekistan for publishing the main scientific results of thesiss.

Structure and length of the thesis: The dissertation consists of an introduction, five chapters, and a conclusion, followed by a list of 265 references. Its total length is 122 pages and it includes 41 figures and 3 table.

MAIN CONTENT OF DISSERTATION

In the Introduction, the dissertation substantiates the importance and relevance of the research topic, formulates the aim and objectives, delineates the object, subject, and methods of investigation, and articulates the study's alignment with the priority areas of scientific and technological development of the Republic of Uzbekistan. It further defines the scientific novelty and practical significance, demonstrates data reliability, outlines implementation and approbation, and presents the overall structure of the dissertation.

Chapter I provides a critical review of the literature on ADIB with carbon-based cathodes—graphite and binder-free graphene paper. The discussion focuses on $AlCl_4^-$ anion intercalation and staging mechanisms in layered carbon materials. The analysis correlates electrolyte composition and Lewis acidity ($AlCl_3$:[EMImCl] molar ratios) with electrochemical response and highlights structural attributes—high electrical conductivity and accessible interlayer galleries—that enhance reversibility and cycling stability. Advances in cathode modification, interphase control, and electrolyte optimization are synthesized, and existing knowledge gaps are identified to frame the experimental and modeling program.

Chapter II details the materials and methods employed in the study, including the fabrication of graphite-on-carbon-paper electrodes using λ-carrageenan as a binder with carbon black and the preparation of binder-free graphene paper cathodes. The section also describes the formulation of rigorously anhydrous $AlCl_3$:[EMImCl] electrolytes at varied molar ratios, along with the standardized procedures for CV, EIS, GCPL tests—specifying potential windows, scan rates, and normalization protocols. Structural and interfacial characterizations using XRD, Raman spectroscopy, SEM/EDS, are described with key analytical parameters. A COMSOL Multiphysics workflow is introduced to couple ionic transport with chemo-mechanical responses in graphene-paper cathodes.

Chapter III "Electrochemical measurement and results for graphene paper and graphite cathodes in ADIB" presents the experimental results figure-by-figure, correlating electrochemical behavior with electrolyte acidity, cathode architecture, and coupled transport–mechanical effects. For instance,

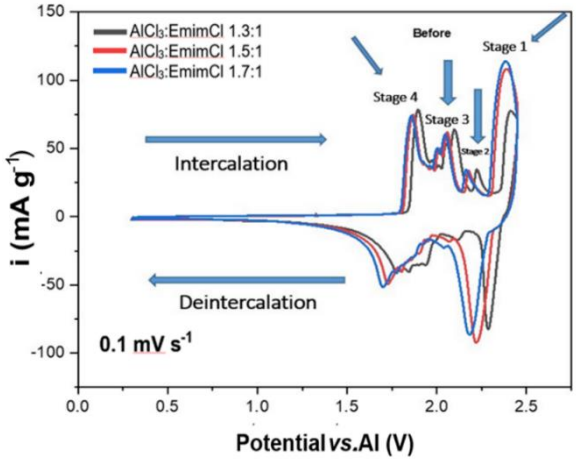


Figure 3.1. CV of graphite in $AlCl_3$:[EMImCl] (1.3:1–1.7:1): staged $AlCl_4^-$ intercalation and reduced hysteresis with acidity

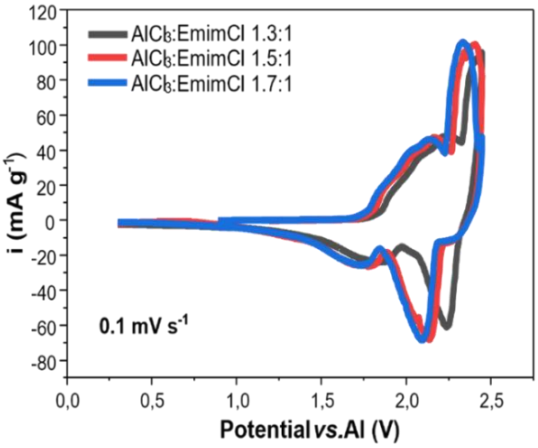


Figure 3.2. CV analysis of graphene paper: variation of staging with increasing acidity

Figure 3.1, which shows the CV of graphite with $AlCl_3$:[EMImCl] ratios of 1.3:1 (black curve), 1.5:1 (red curve), and 1.7:1 (blue curve) (0.30–2.45 V vs Al), reveals a clear multistep staging sequence with well-matched cathodic counterparts. Increasing Lewis acidity sharpens and separates the peaks, contracts anodic–cathodic offsets, and maintains a flat inter-peak baseline. Anodic features are observed at approximately 2.03, 2.20–2.26, 2.31–2.35, and 2.42–2.45 V (Stage-1 onset), with cathodic counterparts shifted by ~ 30–70 mV. Peak currents increase (from 60 to 110 mA· g^{-1}), while hysteresis decreases (from 80 to 100 mV, approximatel 30–50 mV), indicating higher exchange current density (i_0) and reduced charge-transfer and mass-transport limitations. Figure 3.2 presents overlaid CV peaks of the graphene paper electrode in $AlCl_3$:[EMImCl] electrolytes, exhibiting a strictly monotonic response to increasing acidity. The anodic staging transitions shift slightly toward higher potentials - Stage 4: ~2.05 → 2.07–2.09 V, Stage 3: ~2.20–2.23 → 2.23–2.26 V, Stage 2: ~2.31–2.33 → 2.34–2.36 V, and the Stage 1 onset at ~2.43–2.45 V—with corresponding cathodic returns appearing ~30–70 mV lower. The peaks become narrower (FWHM decreases by ~20–35%) and more intense (terminal i_p increases from around 100 to 115 and approximately to 130–140 mA· g^{-1} for 1.3:1, 1.5:1, and 1.7:1 ratios, respectively), while the inter-peak baseline remains flat ($|i| \leq 1–2$ mA· g^{-1}). No capacitive envelope is observed across repeated or scan-rate tests. The reduced ΔE_p (~30–50 mV) and improved peak symmetry indicate a higher i_0 and a narrower energy-barrier distribution at the GP/electrolyte interface, consistent with acidity-driven chloroaluminate speciation.

Figure 3.3 shows Galvanostatic profiles at a current density of 25 mA· g^{-1}which reproduces CV-resolved staging (dV/dQ matches within a few mV), with discharge at ~1.95–2.05 V and charge at around 2.20–2.25 V. Increasing Lewis acidity

(1.3:1→1.7:1) narrows the gap from 0.25 to 0.15 V, maintains a near-flat baseline, and slightly raises capacity (90→93 mAh· g^{-1}). The smaller iR step and reduced hysteresis indicate lower Rs and diminished η_{ct}; voltage efficiency correspondingly improves and is reproducible across repeats.

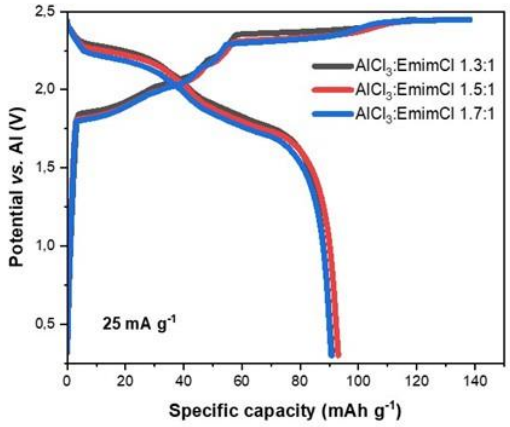


Figure 3.3. GCPL measurement of the graphite cathode

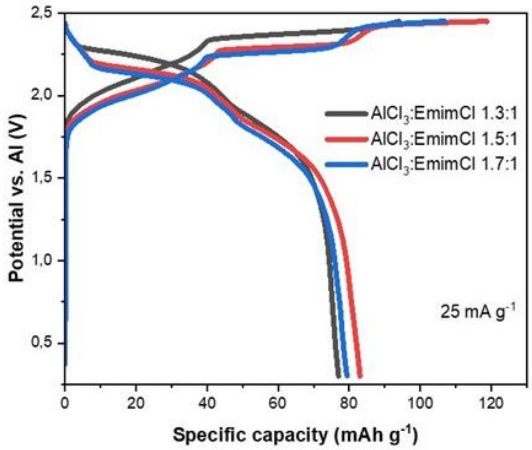


Figure 3.4. GCPL measurement of the graphene paper

As shown in Figure 3.4, binder-free graphene paper shows flatter, distinctly staged plateaus and a smaller charge–discharge gap than laminated graphite. With increasing Lewis acidity (black→red→blue), discharge capacity rises modestly (from 78 to around 82 mAh· g^{-1}) while hysteresis contracts from 0.30–0.33 V to ~0.18–0.20 V. Plateau levels on graphene paper are slightly higher and flatter—discharge at around 1.92–2.02 V; charge at around 2.18–2.23 V—with sharper dV/dQ features. The acidity series narrows peak spacing and smooths inter-plateau transitions, indicating accelerated interfacial kinetics and reduced porous-transport losses in the edge-rich, binder-free graphene paper architecture.

Figure 3.5 (Nyquist, graphene paper). The high-frequency intercept decreases ($\downarrow R_s$) with improved wetting and higher κeff. The mid-frequency depressed arc contracts and shifts to higher characteristic frequency ($\downarrow Rct$, $\uparrow i0$, narrower dispersion; CPE $n\uparrow$). The low-frequency ≈ 45° Warburg tail shows a reduced length and steeper effective slope deviation, indicating $\uparrow D_{\text{eff}}$ and reduced tortuosity. Equivalent-circuit fits R_s – (R_{ct} ∥ CPE) – W thus give monotonic declines in R_s and R_{ct} with a mild increase in interfacial capacitance—consistent with CV peak sharpening, plateau alignment, and reduced GCPL hysteresis.

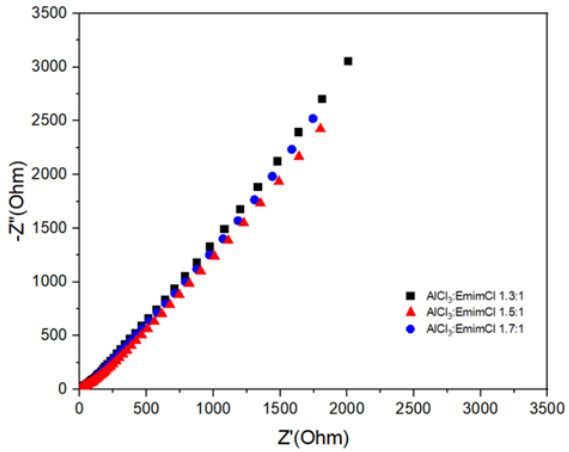


Figure 3.5. EIS analysis of the graphene paper

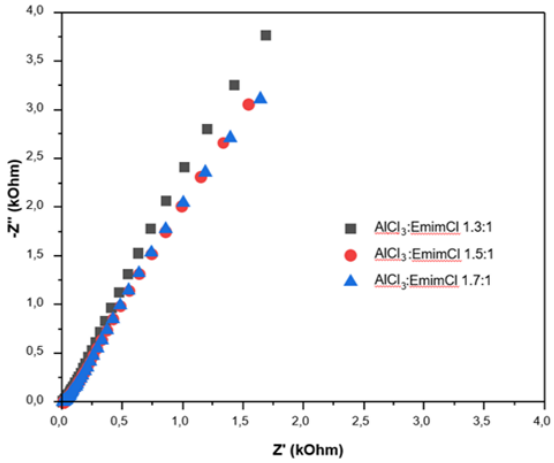


Figure 3.6. EIS analysis of the graphite cathode

Figure 3.6 (Nyquist, graphite) follows the same acidity trend as graphene-paper-decreasing R_s, a shrinking, faster mid-frequency arc, and an approximate 45° Warburg tail-but at uniformly higher impedances. Fits to R_s – (R_{ct} ‖ CPE) – W yield larger R_s (poorer wetting/κ_{eff}), larger R_{ct} (smaller i_0), and lower CPE exponent n, all improving monotonically with acidity. Even at the highest acidity, R_s and R_{ct} only approach (not match) graphene-paper, and the Warburg slope stays steeper-consistent with higher tortuosity and fewer edge pathways-implicating speciation-controlled kinetics as the main lever while electrode architecture fixes the baseline and residual gap.

Figure 3.7 shows rate performance of graphite in three $AlCl_3$:[EMIm]Cl ratios: capacity drops with current for all, but 1.7:1 exhibits capacity of around 85 mAh· g^{-1} at 25 mA· $g^{-1}$and 10–15 mAh· g^{-1} at 500 mA· g^{-1} with shortened plateaus and larger ΔV yet unchanged intercalation voltages (kinetic, not thermodynamic limits). Capacity fully recovers to 85 mAh· g^{-1} when the current returns to the 25 mA· g^{-1}, indicating reversible polarization. Consistent with EIS/CV, the 1.7:1 electrolyte shows highest κeff and i_0, yielding the best retention and smallest ΔV rise at high rates.

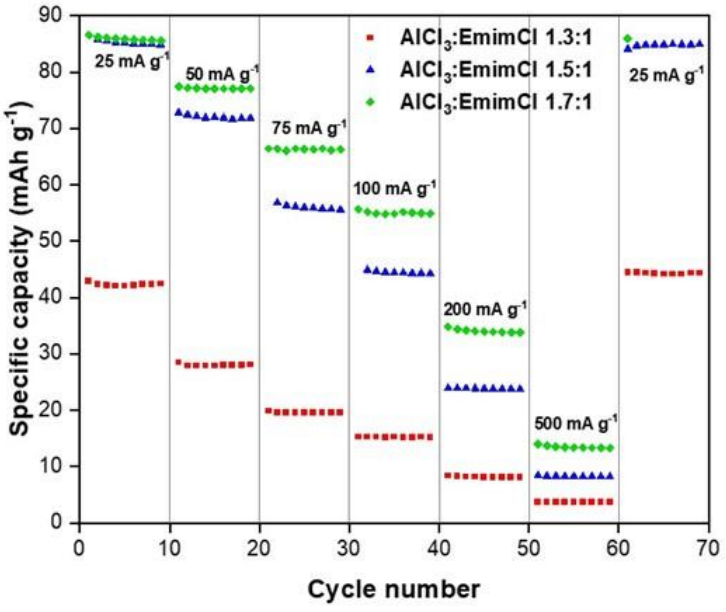


Figure 3.7. Rate capability performance of the graphite cathode at different electrolyte molar ratios

Figure 3.8 (graphene paper) shows higher capacities than graphite at all currents and ratios. At the current density of 25 mA· g^{-1}, it delivers capacities of 76 (1.3:1), ~78 (1.5:1), and ~ 82 mAh· g^{-1} (1.7:1) recpectively, exceeding graphite under identical conditions. At the current density of 500 mA· g^{-1}, retention remains superior: around 27 (1.7:1) > ~22 (1.5:1) > 10 mAh· g^{-1} (1.3:1) respectively. Thus, 1.7:1 provides the fastest kinetics for both electrodes, while graphene papers conductive, porous architecture yields higher absolute capacity and better rate capability. Full recovery upon returning to current density 25 mA· g^{-1} confirms reversible polarization rather than degradation.

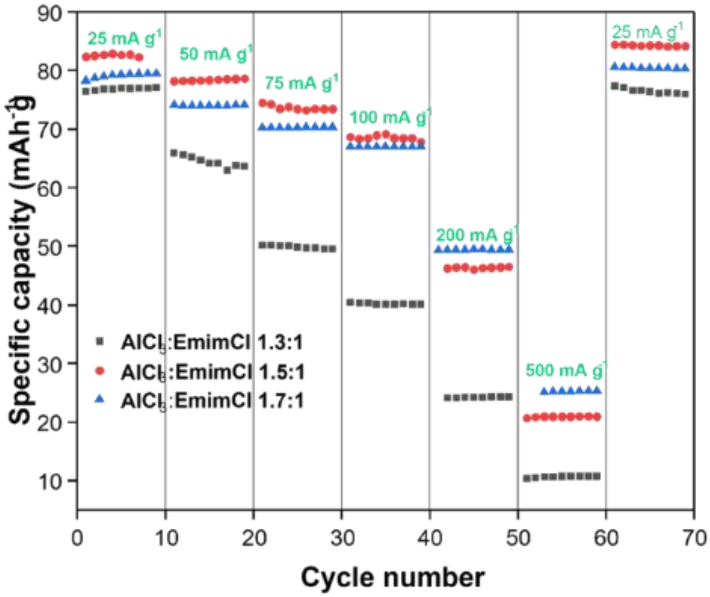


Figure 3.8. Rate capability performance of the graphene paper at different electrolyte molar ratios

Figure 3.9a (1.3:1, 100 mA g^{-1}) shows graphene paper stabilizing at the capacity of 80 mAh· g^{-1} with CE rising to around 99–100% for 500 cycles; the small charge–discharge gap indicates low parasitics and a stable interphase. In Figure 3.9b (1.5:1), capacity fades from discharge capacity from 35 to ~ 25 mAh· g^{-1} while CE rises from approximately 80 to ~99%, reflecting potential transport/kinetic issues or interphase formation. Figure 3.9c (1.7:1) shows stable capacity of 70 mAh· g^{-1} and CE ≈100%, confirming durability. Higher Lewis acidity (1.7:1) improves charge transfer and transport compared to 1.5:1, but 1.3:1 shows highest capacity, possibly due to optimal $AlCl_4^-$ concentration for intercalation despite lower kinetics.

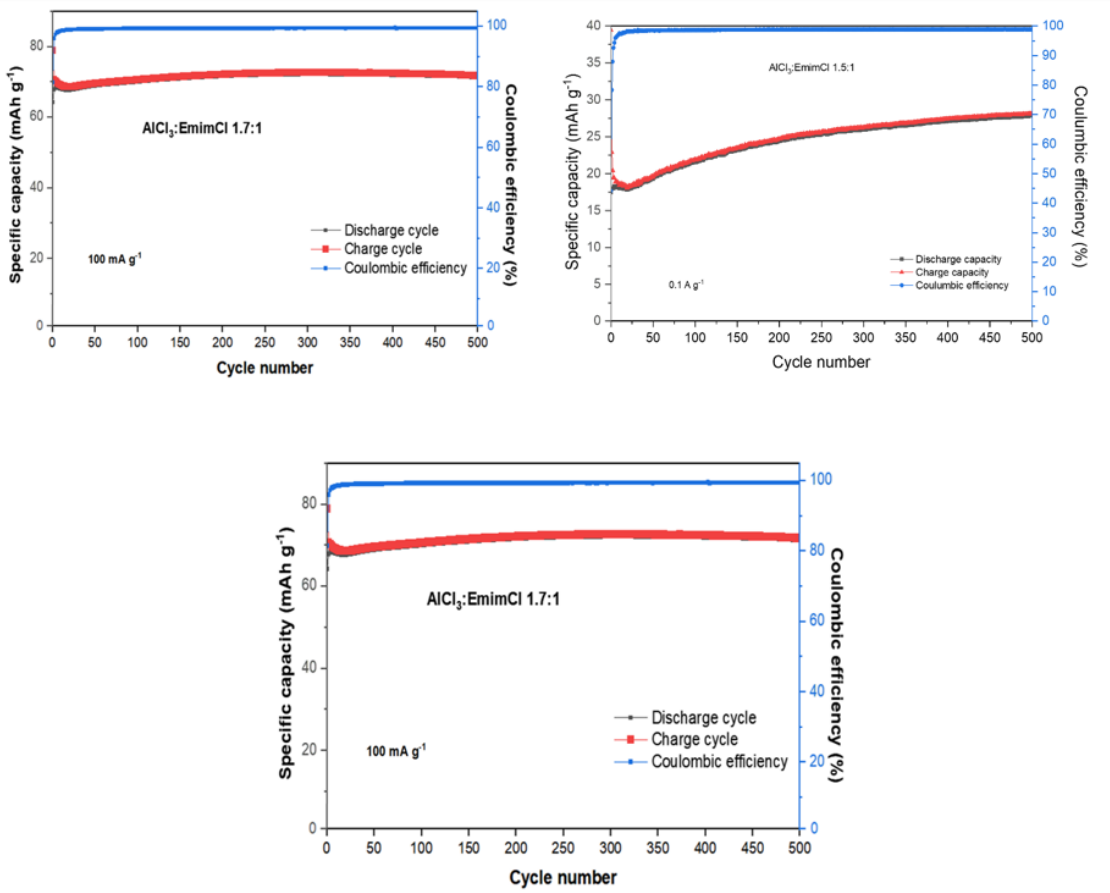


Figure 3.9. Long-term stability test of the graphene paper electrode

As demonstrated in Fig. 3.10a and further supported by Fig. 3.10b—the binder-free graphene-paper pouch cell in the 1.7:1 electrolyte shows reversible rate behavior and long-term stability. In Fig. 3.10a, capacities decrease with increasing capacity (from ~180 mAh· g^{-1} at current density of 11 mA· g^{-1} to near-zero at 229 mA· g^{-1}) and partially recover upon returning to current density of 11 mA g^{-1} (~150 mAh· g^{-1}), with CE fluctuating around 95–100%, indicating transport-limited polarization without irreversible degradation. Fig. 3.10b shows stable cycling at constant current density of 11 mA· g^{-1} over ~160 cycles, with CE near unity after initial formation and gradual capacity fade (from 120 to nearly 80 mAh· g^{-1}), confirming high reversibility and a stable interphase under mild kinetic conditions.

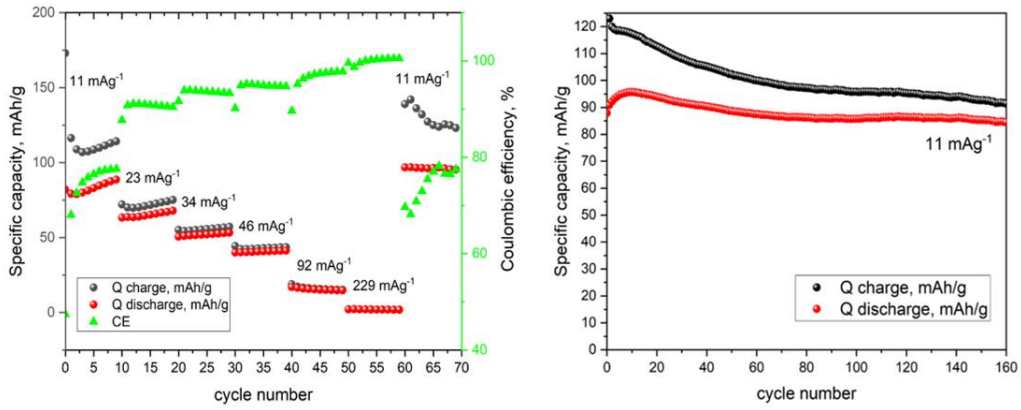


Figure 3.10. Rate capability and stability test of the pouch-structured graphene paper.

Chapter IV "Post mortem analysis of graphene paper" In Figure 4.1, the XRD data confirms that all three materials—GP-120, GP-35, and graphite—possess a hexagonal graphitic structure with high phase purity, as evidenced by the (002) peak at ~12° (2θ; $d_{002} \approx 3.35$ Å) and in-plane reflections. GP-120 stands out as the most suitable for ADIB cathodes due to its combination of sharp, symmetric peaks, moderate (002) broadening, and minimal turbostratic disorder, which suggest a robust framework with sufficient edge exposure for efficient ion-exchange kinetics. While graphite exhibits the highest crystallinity, GP-120 offers a practical microstructural compromise, outperforming GP-35, which shows greater disorder.

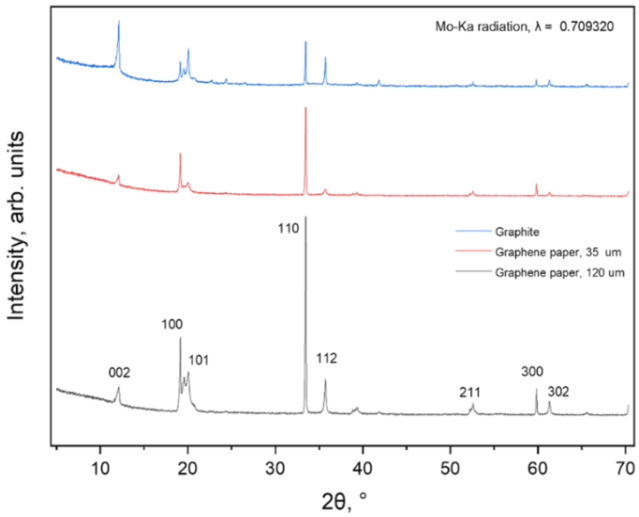


Figure 4.1. XRD patterns of graphene paper and graphite electrodes before cell assembly

In Figure 4.2, ex-situ XRD patterns for the $AlCl_3$:[EMImCl] = 1.3:1 electrolyte are presented in two 2θ windows: the low-angle region (5–15°) emphasizes the evolution of the graphitic (002) reflection, while the wide-angle range (10–55°) highlights additional weak and broad features associated with electrolyte-derived components. After 500 cycles, the (002) peak remains identifiable but exhibits pronounced broadening and an elevated diffuse background, signifying increased microstrain, turbostratic disorder, and partial amorphization of the carbon

framework under the lower-acidity condition. Importantly, no new intense Bragg reflections appear throughout the scanned range, confirming the absence of bulk crystalline decomposition products despite the higher structural disorder accumulated during cycling.

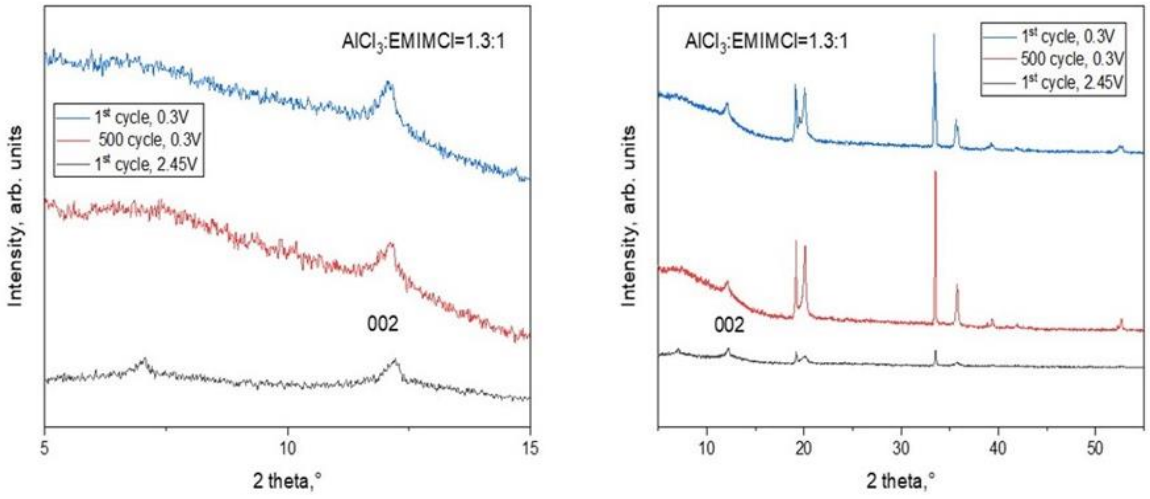


Figure 4.2. XRD patterns at initial and long-term cycles in the 1.3:1 electrolyte

In Figure 4.3, the $AlCl_3$:[EMImCl] = 1.5:1 electrolyte exhibits a more reversible (002) response compared to the 1.3:1 system. Upon recharge, the (002) reflection shifts closer to its original pristine position with a narrower full width at half maximum (FWHM) and a lower diffuse background, indicating reduced turbostratic disorder and microstrain within the graphite layers. In the wide-angle region (10–55°), the residual broad features associated with electrolyte-derived products are noticeably weaker and less persistent after extended cycling. The absence of new sharp Bragg reflections confirms that the interphase remains structurally stable, with minimal by-product accumulation under this intermediate Lewis acidity.

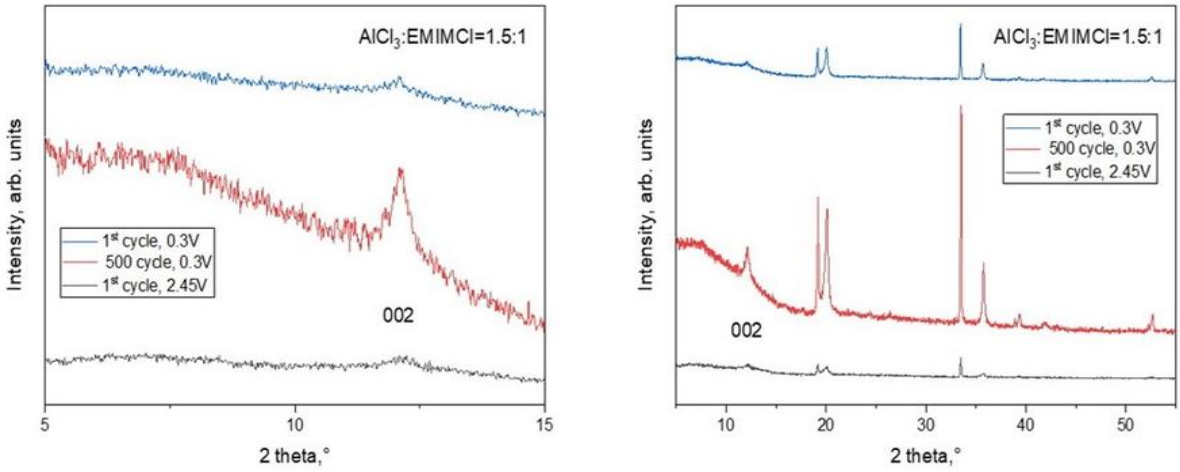


Figure 4.3. XRD patterns at initial and long-term cycles in the 1.5:1 electrolyte

In Figure 4.4, the $AlCl_3$:[EMImCl] = 1.7:1 electrolyte exhibits the sharpest and most reversible graphitic (002) response among the tested compositions. The (002) peak shows the narrowest full width at half maximum (FWHM) and undergoes a well-defined, reproducible shift during intercalation and de-intercalation, returning

nearly to its pristine position with minimal residual broadening. After 500 cycles, both the low-angle and wide-angle regions retain a low diffuse background and display few, if any, persistent extra reflections, confirming a clean, stable interphase and negligible buildup of crystalline by-products. These results demonstrate that higher Lewis acidity promotes superior structural reversibility, reduced disorder, and enhanced phase cleanliness in the graphite cathode.

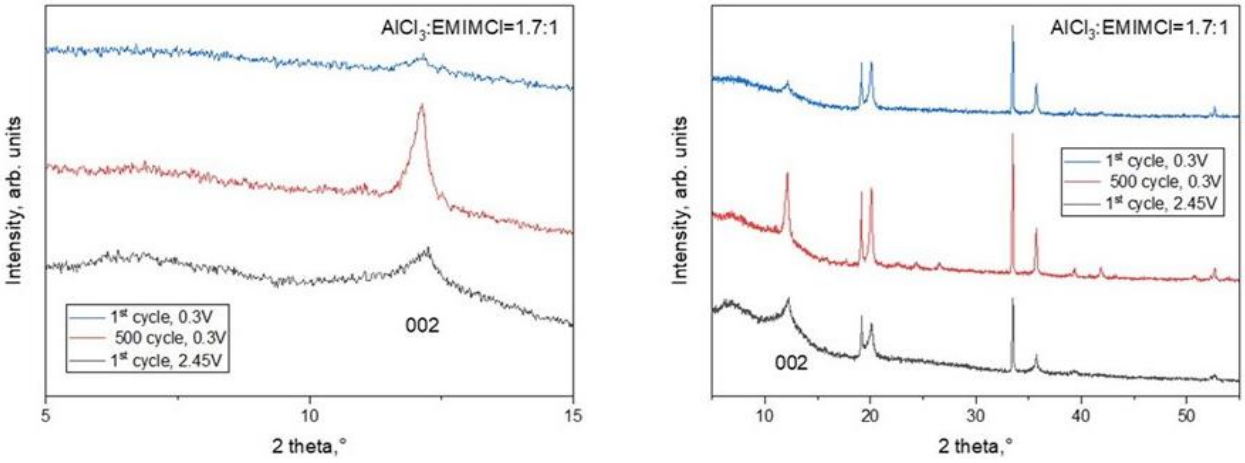


Figure 4.4. XRD patterns at initial and long-term cycles in the 1.7:1 electrolyte

In Figure 4.5, Raman spectra collected at 0.3 V (first discharge) for $AlCl_3$:[EMImCl] melts of increasing Lewis acidity (1.3:1 → 1.5:1 → 1.7:1) display a systematic p-doping trend. With higher $AlCl_3$ content, the G-band upshifts and slightly narrows, the 2D band weakens, broadens, and downshifts marginally, while the intensity ratio I_D/I_g remains low but increases modestly.

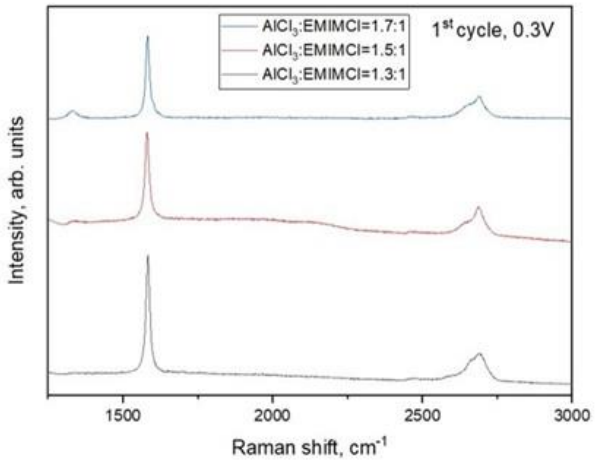


Figure 4.5. Raman spectra of graphene paper and electrolytes with different molar ratios at the first cycle (0.3 V)

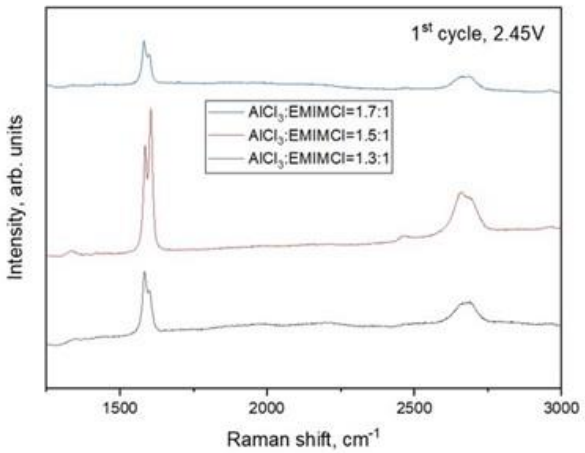


Figure 4.6. Raman spectra of graphene paper and electrolytes with different molar ratios at the first cycle (2.45 V)

These concurrent shifts indicate enhanced anion – π charge transfer and staging at higher Lewis acidity, consistent with stronger electronic interaction between $AlCl_4^-$ and the graphitic layers. The stable, low I_D/I_G ratio further confirms that this interaction proceeds without substantial lattice damage, reflecting effective p-doping and structural integrity of the graphite framework.

In Figure 4.6, Raman spectra recorded at 2.45 V (first charge) exhibit a distinct G-band upshift accompanied by clear splitting, corresponding to charged and

uncharged graphitic planes. Concurrently, the 2D band shows strong attenuation and pronounced broadening—hallmark features of acceptor-type staging and substantial π-band hole doping induced by $AlCl_4^-$ intercalation. These effects are most pronounced for the 1.7:1 melt, signifying deeper and more ordered staging with enhanced charge transfer at higher Lewis acidity. Importantly, the I_D/I_G ratio remains nearly constant, indicating that this strong electronic interaction occurs without significant defect formation. The Raman behavior correlates closely with the XRD observations, where the 1.7:1 system likewise demonstrates the sharpest and most reversible (002) evolution, confirming structurally coherent intercalation–deintercalation dynamics.

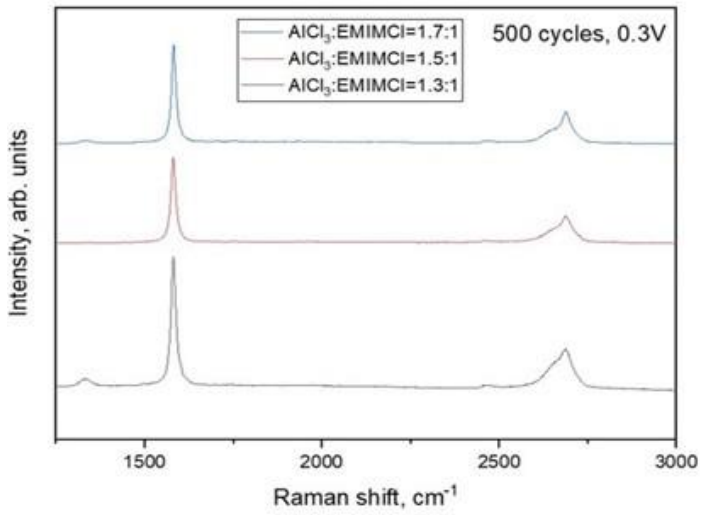


Figure 4.7. Raman spectra of graphene paper and electrolytes with different molar ratios after 500 cycles

In Figure 4.7, Raman spectra acquired after 500 cycles at 0.3 V reveal that the G band relaxes toward its pristine position, while the I_D/I_G ratio remains consistently low-most notably for the 1.7:1 electrolyte-signifying minimal permanent disorder and partial reversal of p-doping upon $AlCl_4^-$ deinsertion. The 2D band remains clearly visible with only slight broadening, and no new defect-activated bands appear. These observations confirm the preservation of graphitic order and the formation of a chemically stable interphase even after prolonged cycling, highlighting the structural resilience of the graphite cathode under high-Lewis-acidity conditions.

In Figure 4.8, ex-situ SEM images of the graphite cathode after extended cycling to 0.3 V reveal a pronounced dependence of surface morphology on electrolyte acidity. In the 1.3:1 melt, the electrode surface is partially masked by discontinuous, film-like deposits consistent with electrolyte-derived residues. At 1.5:1, the morphology becomes rougher and more heterogeneous, exhibiting localized overgrowths and patchy surface coverage. In contrast, the 1.7:1 electrolyte preserves the underlying lamellar texture of the graphite with cleaner edges and significantly reduced particulate debris. This progressive improvement in surface definition and cleanliness with increasing Lewis acidity indicates the formation of a more stable, self-limiting interphase and the suppression of parasitic deposition processes in the 1.7:1 system.

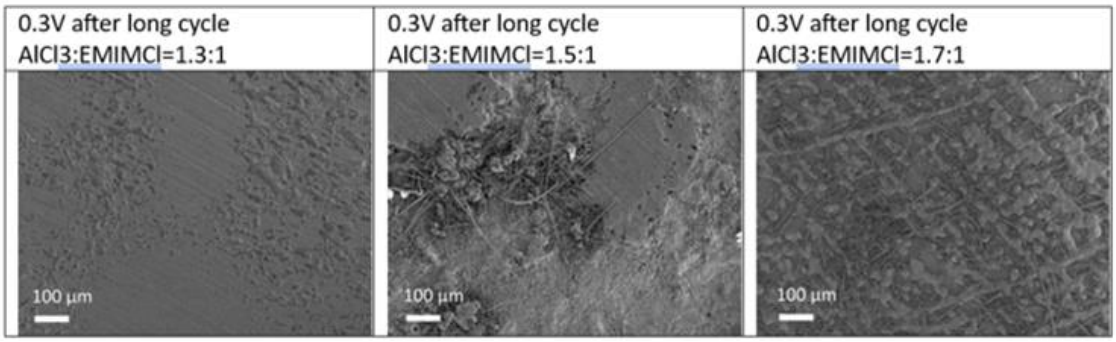
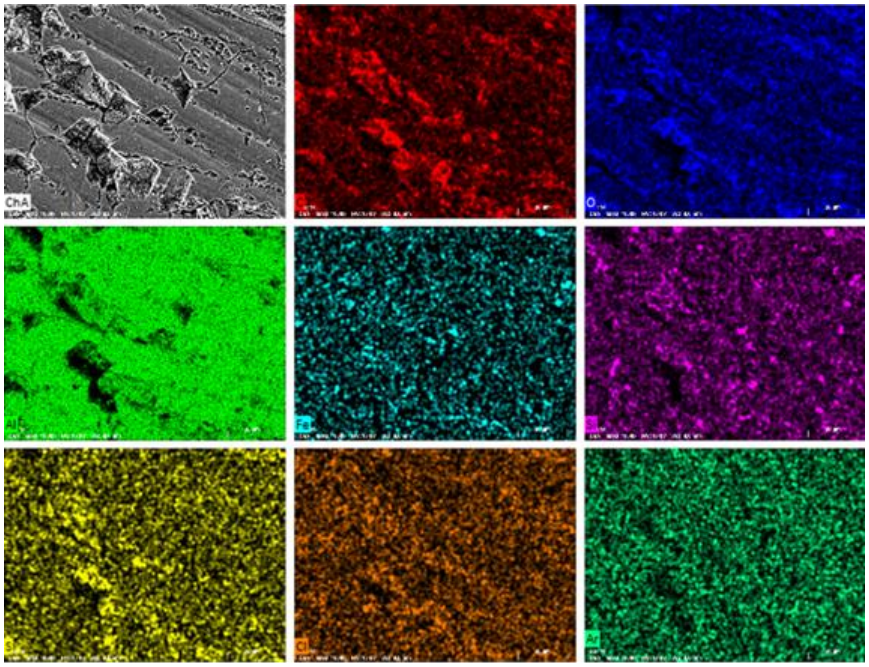


Figure 4.8. SEM images of graphene paper after long-term cycling in electrolytes of different molar ratios



Element	Atomic No.	Net Counts	Mass %	Mass % (Norm.)	Atoms %	Abs. Error (Mass%)	Rel. Error (%)
Carbon	6	22 556	5.95	10.50	20.74	±0.31	5.25
Oxygen	8	20 584	1.30	2.29	3.39	±0.05	4.13
Aluminium	13	2 206 803	48.33	85.27	74.97	±1.41	2.92
Argon	18	2 065	0.16	0.27	0.16	±0.01	7.46
Iron	26	1 412	0.88	1.55	0.66	±0.07	8.34
Silicon	14	0	0.00	0.00	0.00	0.00	999.00
Sulfur	16	0	0.00	0.00	0.00	0.00	999.00
Chlorine	17	1 205	0.07	0.12	0.08	±0.01	11.88
Sum			56.68	100.00	100.00		

Figure 4.9. SEM and EDS analyses of graphene paper after long-term cycling

As demonstrated in Figure 4.9a, the SEM–EDS maps show uniform distributions of C, O, Al, and Cl without localized hotspots, indicating the absence of crystalline salts or metal clusters and confirming a thin, conformal CEI layer. As showed in Figure 4.9b, the corresponding EDS spectra are dominated by carbon with minor Al and trace Cl/O signals, consistent with a nanometric CEI containing residual chloroaluminate and oxo-species. These results collectively support the formation of a uniform, chemically thin interphase rather than crystalline deposits.

Chapter V "Comsol multiphysics modeling" In Figure 5.1, a 3D COMSOL chemo-mechanical simulation of laminated graphene paper under galvanostatic operation reveals von Mises stress concentrations primarily at the sheet edges, corners, inter-ply termini, and the current-collector interface, while the interior plies remain comparatively relaxed. These localized stress hotspots originate from nonuniform $AlCl_4^-$ intercalation, which generates eigenstrain gradients through the laminate thickness. Mechanical constraint from the collector translates intercalation-induced dilation mismatch into localized shear and bending stresses. The simulation highlights potential design optimizations—such as introducing compliant, ion-conductive interlayers, smoothing or rounding edge geometries, implementing distributed current take-off, and engineering graded porosity or conductivity—to mitigate stress accumulation and prevent interfacial degradation in graphene paper electrodes.

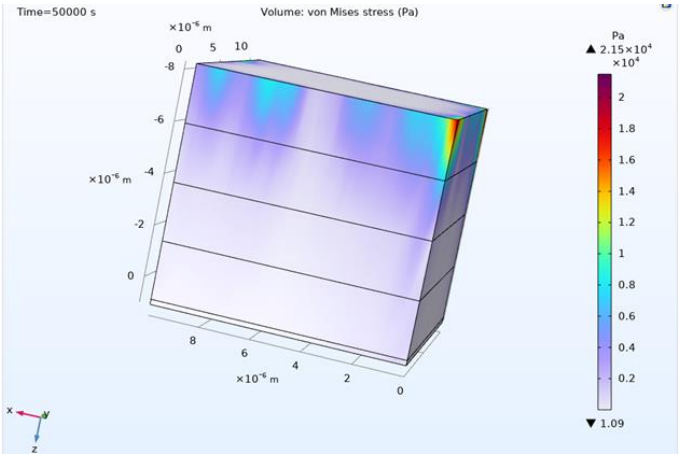


Figure 5.1. COMSOL simulation of von Mises stress distribution in graphene paper under galvanostatic operation

In Figure 5.2, a Rüdorff–Hofmann–style schematic illustrates discrete $AlCl_4^-$ staging in graphene layers (stage n: every nth gallery filled), progressing from sparse to dense intercalation. Each stage is assigned a coverage θ_n and a c-axis dilation coefficient $\alpha c(\theta_n)$, applied as eigenstrain $\varepsilon^*(\theta) = \alpha c(\theta)\, e_{(c)} \otimes e_{(c)}$ in the COMSOL model. Early stages initiate at edges, generating steep $\nabla\theta$ gradients and localized stresses; higher stages distribute more uniformly but elevate overall strain energy. This staging framework correlates electrochemical data (CV peaks, XRD (002) shifts, Raman signatures) with constitutive inputs $\alpha c(\theta)$, $i_0(\theta)$, and $D(\theta)$—enabling predictive chemo-mechanical simulations of multilayer graphene-paper electrodes.

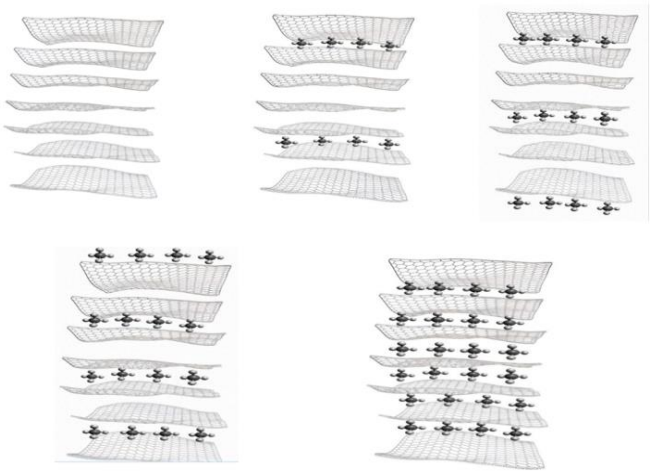


Figure 5.2. Schematic illustration of $AlCl_4^-$ intercalation staging in graphene paper.

Conclusion and outlook

1. The results demonstrate that the electrode architecture and the $AlCl_3$:[EMIm]Cl electrolyte ratio are the primary factors governing the functional performance of the ADIB system. The binder-free graphene paper, with its highly conductive architecture, enabled accelerated ion transport and enhanced reversibility of $AlCl_4^-$ intercalation, delivering superior performance compared with the graphite composite. Among the tested compositions, the electrolyte with a 1.7:1 molar ratio exhibited the most stable long-term cycling, whereas the 1.5:1 system showed elevated performance only during the initial charge–discharge processes. These distinctions confirm the complex yet interconnected roles of ion mobility, Lewis acidity, and interlayer stability in ADIB cells.

2. Swagelok-type Al/graphene and Al/graphite cells were evaluated using CV, EIS, and GCPL measurements. At a current density of 25 $mA \cdot g^{-1}$, the graphite electrode delivered approximately 90 $mAh \cdot g^{-1}$, while the graphene paper showed around 80 $mAh \cdot g^{-1}$. However, at higher current densities, the graphene paper outperformed graphite due to its superior ion and electron transport characteristics. During cycling at 100 $mA \cdot g^{-1}$, the graphene paper stabilized at 70–75 $mAh \cdot g^{-1}$ after 500 cycles and maintained nearly 100% Coulombic efficiency. COMSOL simulations revealed a maximum von Mises stress of ~ 2×10^4 Pa, indicating only minimal deformation and confirming the excellent mechanical robustness of the binder-free graphene paper.

3. XRD spectra of the binder-free graphene paper cathode obtained after charging (2.45 V) and discharging (0.3 V) for the 1st and 500th cycles at different $AlCl_3$:[EMIm]Cl ratios (1.3:1, 1.5:1, and 1.7:1) reveal clear structural differences. Under MoKα radiation, the broad (002) reflection centered around ~12° confirms the turbostratic nature of the graphene paper. After 500 cycles, the 1.7:1 electrolyte system retained a well-defined (002) peak, indicating superior electrochemical stability of this cathode configuration.

4. Ex-situ Raman spectra of the binder-free graphene paper obtained at different $AlCl_3$:[EMIm]Cl ratios (1.3:1, 1.5:1, and 1.7:1) exhibit characteristic features of sp^2-carbon. During charging up to 2.45 V, a slight upshift of the G-band together with an increase in the I_D/I_G ratio indicates reversible lattice stress induced by $AlCl_4^-$ intercalation. After 500 cycles, the 1.7:1 electrolyte composition preserved nearly unchanged Raman features, confirming its superior structural stability. In contrast, the 1.3:1 and 1.5:1 systems show a noticeable enhancement of the D-band, consistent with defect accumulation during prolonged cycling. These results demonstrate that higher Lewis acidity (1.7:1) promotes more stable intercalation and preserves lattice integrity.

5. The optimized 1.7:1 $AlCl_3$:[EMIm]Cl electrolyte, combined with a pouch-type Al/graphene cell geometry, exhibited moderate rate capability and good cycling reversibility. At a current density of 11 $mA \cdot g^{-1}$, the cell delivered approximately 95 $mAh \cdot g^{-1}$ while maintaining a Coulombic efficiency of about 95%. However, a gradual capacity decrease was observed at higher current densities, indicating partial rate limitations associated with sluggish $AlCl_4^-$ diffusion and increased electrolyte viscosity under fast-operation conditions. During long-term cycling, the cell preserved stable performance over approximately 160 cycles. Nevertheless, further optimization of both electrolyte composition and cathode architecture is required to enhance long-term stability and energy efficiency for practical ADIB applications.

НАУЧНЫЙ СОВЕТ DSC.02/30.12.2019.FM/T.65.01 ПО ПРИСУЖДЕНИЮ УЧЕНЫХ СТЕПЕНЕЙ ПРИ ИНСТИТУТЕ ИОННО-ПЛАЗМЕННЫХ И ЛАЗЕРНЫХ ТЕХНОЛОГИЙ

ИНСТИТУТ ИОННО-ПЛАЗМЕННЫХ И ЛАЗЕРНЫХ ТЕХНОЛОГИЙ

АШУРОВ ИЛХОМЖОН ХАТАМ УГЛИ

ЭКСПЕРИМЕНТАЛЬНОЕ ИССЛЕДОВАНИЕ И ВЫЧИСЛИТЕЛЬНЫЙ МЕТОД ГРАФЕНОВОГО КАТОДА И ИОННЫХ ЖИДКИХ ЭЛЕКТРОЛИТОВ ПРИ КОМНАТНОЙ ТЕМПЕРАТУРЕ ДЛЯ АЛЮМИНИЕВЫХ АККУМУЛЯТОРОВ

01.04.12- Физика и технология наноматериалов

АВТОРЕФЕРАТ
диссертации доктора философии (PhD) по физико-математическим наукам

ТАШКЕНТ – 2025

Тема диссертации доктора философии (PhD) по техническим науккам зарегистрирована в Высшей аттестационной комиссии при Министерстве высшего образования, науки и инноваций Республики Узбекистан за номером № B2025.3.PhD/FM1385.

Диссертация выполнена в Институте ионно-плазменных и лазерных технологий им. У.А.Арифова АН РУз.

Автореферат диссертации на трех языках (узбекский, русский, английский (резюме)) размещён на на веб-странице Научного совета (www.iplt.uz и на Информационно-образовательном портале «Ziyonet» по адресу (www.ziyonet.uz.)

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Защита диссертации состоится «11» декабря 2025 г. в 14:30 часов на заседании Научного совета DSc.02/30.12.2019.FM/T.65.01 по присуждению учёных степеней при Институте ионно-плазменных и лазерных технологий АН РУз (адрес: 100125, г. Ташкент, ул. Дурмон йули, 33. Тел./Факс: (99871) 262–32–54, e-mail: info@iplt.uz.

С диссертацией можно ознакомиться в Информационно-ресурсном центре Института ионно-плазменных и лазерных технологий (зарегистрирована за № 21). Адрес: 100125, г. Ташкент, ул. Дурмон йули, 33. Тел.: (99871) 262–31–69).

Автореферат диссертации разослан «02» декабря 2025 года.
(Реестр протокола рассылки 21 от «02» декабря 2025 года).

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ВВЕДЕНИЕ (аннотация диссертации на соискание ученой степени доктора философии (PhD))

Цель исследования: разработать механистически обоснованного научного подхода к оптимизации алюминиевых дуал-ионных аккумуляторов (АДИА) путём комплексного изучения кислотности электролита, ионного состава, архитектуры углеродного катода и межфазной стабильности на границе катод–электролит.

Задачи исследования:

- изготовить катоды на основе безсвязующего графеновой бумаги и графитового композита, сравнить их электрохимические свойства и проанализировать механизм интеркаляции для выбора оптимального катодного материала.;
- получить ионные жидкие электролиты $AlCl_3$:[EMIm]Cl в молярных соотношениях 1.3:1, 1.5:1 и 1.7:1 и оптимизировать их свойства путём управления кислотностью Льюиса и формированием ионных видов;
- собрать алюминий/графеновые и алюминий/графитовые ячейки в конфигурациях Swagelok и pouch-cell и исследовать их методом CV, EIS и GCPL;
- изучить механизм интеркаляции ионов $AlCl_4^-$ с помощью ex-situ XRD, отслеживая расширение межслоевых расстояний и формирование выраженной стадийности.;
- провести анализ структурных и механических изменений методом ex-situ Raman, оценить возникающие напряжения вследствие межслоевого расширения и осуществить моделирование в COMSOL Multiphysics;
- разработать прототипы pouch-cell на основе оптимизированных результатов Swagelok-ячеек и интегрировать их в комплексный анализ;
- сформировать практические рекомендации по проектированию, связывающие состав электролита и архитектуру катода для последующего масштабирования (scale-up) АДИА.

Объект исследования: Ионные жидкие электролиты $AlCl_3$:[EMImCl], графитовые и безсвязующие графеновые катоды, а также лабораторные алюминиевые дуал-ионные ячейки в конфигурациях Swagelok и пакетной ячейки (pouch cell).

Научная новизна исследования:

- впервые коммерчески доступная графеновая бумага без связующего применена в качестве катодного материала в ADIA, что позволило исключить неактивные компоненты и отказаться от сложной многоступенчатой технологии приготовления электродов;
- впервые выполнена систематическая электрохимическая оценка катодов из графеновой бумаги и графитового композита в ионных жидких электролитах $AlCl_3$:[EMIm]Cl различных молярных соотношений. Установлены фундаментальные закономерности взаимодействия электрод–электролит и определён оптимальный состав электролита

- впервые результаты ex-situ XRD и Raman были интегрированы с вычислениями модуля Solid Mechanics в COMSOL Multiphysics, что позволило количественно оценить структурные изменения и механические напряжения, возникающие в катоде при циклировании;
- впервые на основе моделирования и эксперимента разработана оптимизированная структура ячейки, которая стала значимым шагом в создании пакетной ячейки АДИА, сочетающих механическую гибкость и высокую электрохимическую эффективность

Внедрение результатов исследования:

В рамках диссертационных исследований полученные научные результаты были успешно внедрены в проект «Технический регламент по обеспечению стабильности заряд-разрядных процессов аккумуляторных модулей электроскутеров, GCPL-диагностики и продления срока службы» (№ 27/10-2025), разработанный во взаимодействии с ООО «VV-LAND». Указанные решения позволяют определить оптимальное окно состояния заряда аккумуляторов (SoC 40–80 %), повысить стабильность пассивного балансирования элементов, а также обеспечить раннее выявление процессов деградации на основе методов GCPL и EIS. Практическое внедрение данных научно-технических разработок подтверждено официальным документом, предоставленным ООО «VV-LAND».

Статья, посвящённая актуальным проблемам, достижениям и перспективам развития алюминий-ионных аккумуляторов: «Current Challenges, Progress and Future Perspectives» (Applied Solar Energy, 2022, Vol. 58, No. 3, pp. 334–354. DOI: 10.3103/S0003701X22030033), была процитирована международными исследователями в ряде работ, включая: J. Chai et al. (Energy Storage Materials, 81, 2025), H. Zhao et al. (Advanced Functional Materials, 2025), R. Afian et al. (Journal of the Physical Society of Indonesia, 1, 2025), A. Borozdin et al. (Russian Metallurgy, 2, 2025), Y. Zhou et al. (Energy Technology, 13(4), 2024) и M. Saghir et al. (Applied Solar Energy, 60(3), 2024).

Структура и объём диссертации: Диссертация состоит из введения, пяти глав, заключения и списка из 265 использованных источников. Общий объём диссертации составляет 122 страниц, содержит 41 рисунок и 3 таблиц.

E’LON QILINGAN ISHLAR RO‘YXATI
LIST OF PUBLISHED WORKS
СПИСОК ОПУБЛИКОВАННЫХ РАБОТ

I bo‘lim (част I; part I)

1. I.Ashurov, M. Adilov. Kh. Ashurov. Undestanding the influence of electrolyte optimization of graphene paper cathodes on the electrochemical performance of aluminum-dual ion batteries. Applied Solar Energy, 2024, Vol. 60, No. 5, pp. 727–735.
2. I.Ashurov, Sh. Iskandarov, M. Adilov. Kh. Ashurov. Current challenges, Progress and Future Perspectives of aluminum ion batteries. Applied Solar Energy, 2022, Vol. 58, No. 3, pp. 334–354.
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5. I.Ashurov, Sh. Iskandarov, M. Adilov. Kh. Ashurov. Evaulating cycle stability in aluminum-graphite battery systems: Current insights and prospective improvements. NamDU Ilmiy Axborotnomasi. 2024, No. 10, pp. 49-52.

Part II (II бўлим, II часть)

6. I.Ashurov, M.Adilov, Kh.Ashurov. “The development of carbon based cathode materials for aluminum ion batteries”. Post Lithium Storage Cluster of Excellence, 2023, Karlsruhe
7. I.Ashurov, U. Choriev, A.Avvalboev, Sh.Iskandarov, T.Turdaliev, Kh.Ashurov, M.Kurbanov. First Internation Conference on low dimensional advanced materials, ICLODAM-24, 2024, Tashkent
8. Kurbanov M.Sh., Akhunov Kh.Kh, Andriyko L.S., Ashurov I.Kh., Avvalboev A.A., Zokhidov Kh. Kh. Silica based lithium ion battery anode nanomaterial. International research and practice conference “Nanotechnology and nanomaterials” August, 2023, Ukraine
9. I.Kh.Ashurov, M.Adilov, Kh. Ashurov. “Electrochemical investigation of carbon-based cathodes for aluminum dual-ion batteries”. International conference on advanced materials and energy storage systems. May 21-23, 2025, Tashkent